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VOLUME I:

KEYNOTE PRESENTATIONS
FEATURE PRESENTATIONS
PANEL PRESENTATIONS
AIR QUALITY RESEARCH
WATER QUALITY RESEARCH

THE CHALLENGES OF A NEW DECADE

November 19 & 20, 1990
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PROCEEDINGS

ENVIRONMENTAL RESEARCH:
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VOLUME 1

KEYNOTE PRESENTATIONS

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AIR QUALITY RESEARCH

WATER QUALITY RESEARCH

Sponsored by

Research and Technology Branch

Environment Ontario

Ontario, Canada

Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1990 Technology Transfer Conference are published in two volumes of conference Proceedings corresponding to the following sessions:

VOLUME I:	KEYNOTE PRESENTATIONS FEATURE PRESENTATIONS PANEL PRESENTATIONS AIR QUALITY RESEARCH WATER QUALITY RESEARCH
VOLUME II:	KEYNOTE PRESENTATIONS FEATURE PRESENTATIONS PANEL PRESENTATIONS LIQUID & SOLID WASTE RESEARCH ANALYTICAL METHODS ENVIRONMENTAL SOCIO-ECONOMICS MULTIMEDIA CONTAMINANTS & BIOTECHNOLOGY

Volume I is comprised of presentations given during Session A and Session B of the conference, as well as all Keynote, Feature, and Panel Presentations.

For reference purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573

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The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

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KEYNOTE PRESENTATIONS

Keynote Paper I

Sustainable Development: The Technological Challenge

Noel J. Brown, Director, United Nations Environment Programme, North America

PAPER NOT AVAILABLE AT TIME OF PRINT

"RESPONSES TO GLOBAL CHANGE:
the Coming Environmental and Economic Revolutions"

Keynote address: J. P. Bruce

Environmental Research: Technology Transfer Conference
Toronto, 19-20 November 1990

Extended Abstract:

The Intergovernmental Panel on Climate Change has provided in 1990, the most definitive scientific assessment to date of the changes in greenhouse gas concentrations in the atmosphere and the probable effects on the world's climate. This consensus report of more than 300 scientists from many countries, places the major conclusions in 4 main categories of descending degrees of scientific certainty. The Panel is certain that in the atmosphere and that human activities are substantially increasing greenhouse gas concentrations in the atmosphere and that the natural radiation exchanges known as the "greenhouse effect", are real. They "calculate with confidence" that CO2 has caused and will continue to produce more than half of the human-enhanced greenhouse effect, and that the long-lived gases, (CO2, nitrous oxides and the CFC's) would require immediate emission reductions of more than 60% to stabilize atmospheric concentrations at present levels. They predict, based on current model results, that if nothing is done, i.e. a "business-as-usual" scenario prevails, global mean temperatures will rise 0.3 degrees C per decade (with a range of 0.2 to 0.5 degrees C) and sea level will rise 6 cm per decade (range 3-10cm) over the next century. These are rates greater than ever experienced since man first tilled the soil, some 10,000 years ago. Northern latitudes and large land areas, like central and northern North America, are predicted to warm more rapidly than the global mean. The impacts of such changes on coastal communities, small islands, water resources, agriculture, forestry, the spread of tropical diseases, would be increasingly profound over the next 100 years. At their lowest level of certainty, they advise that their judgement is that the mean global temperature has already risen 0.3 degrees to 0.6 degrees C over the past 100 years, "broadly consistent with predictions of climate models".

Responses to this prospect have, on the one hand, been widespread alarm, especially on the part of low lying island countries and ones with extensive low coastlines, and countries with only marginal agriculture and water resources. Spokesmen for other countries, such as USSR, see a somewhat warmer climate as mostly advantageous. A number of western European countries, and scattered sub-national jurisdictions elsewhere have already announced plans to cut CO2 emissions, and some, including Canada, have committed themselves to a stabilization of emissions.

However, most agree that concentrated, coordinated international actions are needed to really reduce the rate of accumulation of greenhouse gases and attention is now focussed on negotiation of a global convention on climate change, hopefully by the item of the UN Conference on Environment and Development in Brazil, June 1992. The urgency is great, since as the IPCC points out, if nations can cut CO2 emissions by 2% per annum beginning in 1990, concentrations will be stabilized at 390 parts per million by 2020 or so, but if cuts are delayed 20 years, stabilization will not occur until 2070, and then at a much higher 460 ppm.

There are four major contentious issues which will have to be resolved in negotiations of a Convention on Climate Change. These are:

1) a plan to cut greenhouse gas emissions, especially CO2;
2) a plan to move from net global deforestation to afforestation;
3) transfer of funds or other economic incentives to permit developing countries to make the necessary investments and adjustments, and
4) transfer to developing countries on a preferred basis, of low emission technologies.

All of these issues have potentially enormous economic as well as environmental implications.

The first will require, above all, a major change in energy policies of the nations, especially the highest per capita energy users, Canada and USA. The key requirements are aggressive conservation strategies driven by end-use oriented services rather than the supply side, and switching to lower CO2 emitting fuels, away from oil and coal. Examples of what is achievable at low net cost in North America and India will be outlined.

In the business world, our major industrial competitors, in Europe and Japan, are already much more energy efficient than North America, and are adopting even greater efficiency measures. There is every reason to fear for the future competitiveness of Canada and USA if energy efficiency is not pursued vigorously in the next few decades.

The third of these issues is one stressed by developing countries in all of the pre-negotiation meetings. Without major initial financial investments, they will be unable to institute the energy efficiency, fuel switching and reforestation measures needed to prevent them from augmenting greenhouse gas emissions at a rapid rate to meet the increasing needs and expectations of their people. Such investments are clearly impossible in a world in which the net financial flow is away from the developing world with low commodity prices and huge debts, to the industrialized countries. This flow must be reversed, or at a minimum a major fund, greatly exceeding the $270 million committed to a CFC replacement fund, will be required to permit the developing countries to be full partners in a world-wide effort to protect the global atmosphere.

The recent success of the world community, in agreeing to a strengthened plan for CFC emission controls to protect the ozone layer under the Montreal protocol lends some optimism to the prospect of a more comprehensive climate change convention. It also buys a little time through CFC reductions to put in place the more difficult CO2, methane and nitrous oxide controls.

However, the major issues on the table can only be resolved if the industrialized countries accept their responsibility to greatly reduce their own greenhouse gas emissions, increase afforestation, and assist developing countries to do the same. Revolutions in our thinking about, and use of, energy, and in our relationships with developing countries are urgently needed if we are to protect the atmosphere of our small planet and the climate it produces.

VOLUME I

FEATURE PRESENTATIONS

A1

WHAT'S THE LATEST ON ACID DEPOSITION IN NORTH AMERICA?

Douglas L. Sisterson

Environmental Research Division
Argonne National Laboratory
Argonne, IL USA 60439

This presentation summarizes the results of the National Acid Precipitation Assessment Program State of Science/Technology Report Deposition Monitoring: Methods and Results (Sisterson et al. 1990). The larger document discusses methods to monitor wet, dry, and droplet deposition in the United States and Canada and provides temporal and spatial analyses for the period 1979-1987. A significant portion of the document addresses the representativeness and completeness of large-scale network deposition data at regional and local scales.

The most complete deposition monitoring results are for wet deposition. Information on dry deposition is insufficient to allow spatial and temporal analyses on a regional scale of the major acidic deposition species and their precursors. Information on droplet deposition (i.e., deposition by interception of cloud water and fog droplets, sometimes called "occult" deposition) is even more recent than that on dry deposition, and little information exists for spatial and temporal analyses except at a few sites.

The areas of maximum wet deposition of individual inorganic chemical species in precipitation are located in the northeastern United States and southeastern Canada, and those locations have not changed significantly in the past decade. The weight of scientific evidence suggests that all analytes except pH or acidity exhibited a decreasing (not statistically significant) trend in deposition and concentration in 1979-1987 for the eastern half of the United States and Canada. Median annual precipitation-weighted concentrations are larger in North America than in remote regions of the world by factors of 9 for SO_4^{2-}, 14 for NO_3^-, 7 for NH_4^+, and 4 for H^+. The average pH of precipitation in remote regions of the world is closer to 5.0 than to 5.6. Excluding precipitation monitoring sites from urban areas and the influence of major local sources causes the integrated wet deposition chemistry estimates to be low.

The finding that sulfur and nitrogen species in precipitation have decreased but pH has not changed is perhaps the single largest surprise of the State of Science Report. A large decrease in calcium and other base cations offsets decreases in acid species in precipitation. The reason for the decrease in calcium is not clear. In part, it can be attributed to changes in agricultural practices, paving of rural gravel highways, and perhaps emission controls; the same emission controls that remove sulfur and nitrogen species from smokestacks may also remove base cations such as calcium that reduce precipitation acidity.

Preliminary results indicate that dry deposition for sulfur is between 0.3 and 0.5 of the wet plus dry deposition at regionally representative sites and is between 0.3 and 0.7 for nitrogen. Most of the dry-deposited sulfur is due to SO_2, with values of 50-90%. Most of the dry-deposited nitrogen is due to HNO_3, with values of 76-88%. The ratio of dry plus wet deposition of sulfur species to that of nitrogen species varies between 4.25 and 0.77.

Concentrations of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ are 5-20 times larger in cloud water at high-elevation sites than in precipitation. Droplet deposition of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ is up to three times wet plus dry deposition in the warm season for high-elevation sites that are frequently in cloud. High-elevation sites above 600 m experienced in-cloud conditions 30-40% of the time during the growing season (April-October). The liquid water content averaged about 0.20 g m^{-3} at most sites.

By using these wet, dry, and droplet deposition data together with anthropogenic emissions and an estimated urban perturbation factor for wet and dry deposition, S and NO_x-N mass budgets were determined (Venkatram et al., 1990). For all of the United States and Canada combined, 39% of anthropogenic SO_x-S emissions were accounted for by wet deposition, 23% by dry deposition, and 4% by droplet deposition, and 34% of the emissions were exported from North America. For NO_x-N, 40% of anthropogenic emissions were accounted for by wet deposition, 26% by dry deposition, and 3% by droplet deposition, and 34% of the emissions were exported from North America. The urban perturbation accounts for 15% of the wet plus dry deposition for the United States and Canada combined.

It is interesting to note that both sulfur and nitrogen species in precipitation in Canada in this study exceed Canadian emissions, probably due to the overall net transport of emissions from the United States into Canada.

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Venkatram, A., D. McNaughton, and P.K. Karamchandan. 1990. Relationships between Atmospheric Emissions, Acidic Deposition, and Air Concentrations. SOS/T Report 8, National Acid Precipitation Assessment Program, Washington, D.C.

A10 Measurement of Semi-Volatile Organic Compounds in Ambient Air; G. Hunt, ENSR, Acton, Massachusetts, USA

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B1

ABSTRACT

Leach, J.H., Ontario Ministry of Natural Resources, Lake Erie Fisheries Station, R. R. #2, Wheatley, Ontario, NOP 2P0. Influence of the zebra mussel, Dreissena polymorpha on water quality of Lake Erie.

The European zebra mussel, Dreissena polymorpha (Pallas), is now well established in the Great Lakes system. Initial colonization may have occurred in 1986, likely from larvae discharged in ballast water, but mussels were not observed in Lake St. Clair and Lake Erie until June 1988. Large populations of the mussel are now established in these lakes. It has spread to all of the Great Lakes and is found from Cornwall, Ontario, in the east to Duluth, Minnesota, in the west. Dispersion has been aided by a motile larval stage and the ability of adults to attach to boat hulls with byssus threads.

The zebra mussel is a serious biofouling pest in Europe and is rapidly becoming one in North America. One of its most harmful impacts is the colonization of intake cribs and pipes serving water treatment plants, power generating stations and industries. Costs associated with prevention of infestations and removal of encrustations are projected at many millions of dollars.

Ecological impacts are also possible but are more difficult to predict and quantify. There is concern that some species of native mussels, and in particular the large unionids, may be in jeopardy because their shells are being colonized to the point where the mussels can no longer function normally. Although impacts on fisheries have not yet been measured, managers are concerned that the invader could affect fish production in two ways. The fouling of spawning reefs could affect reproduction of shoal spawners if the habitat is altered sufficiently to reduce egg deposition and survival. Preliminary results from observations on walleye in the western basin of Lake Erie indicated that reproduction and survival in 1990 were satisfactory. Secondly, the shifting of organic matter from pelagic to benthic areas through filtering by zebra mussels could disrupt the food web that links primary production to larval fish. Research to quantify this process and to determine its impact on the food web is currently underway in Lake Erie.

The zebra mussel has already affected water quality in Lake Erie and Lake St. Clair. The most visual impact is an increase in water clarity. Between 1988 and 1989 (May to November), mean Secchi disc transparencies increased 85 percent and 52 percent in the western and central basins of Lake Erie respectively. Preliminary data to September 1990 indicate that mean transparencies in 1990 were still greater than those in 1988 but less than those recorded in 1989. Resuspension of bottom sediments due to above normal winds during spring and early summer of 1990 probably masked the effects of the zebra mussels on water clarity. For example, transparencies in the western basin in August and September, 1990, were above those measured in the same period in 1989. Turbidity in Rondeau Bay has declined to the point where water clarity is probably sufficient to permit rooted aquatic plants to reestablish.

Mean concentrations of chlorophyll a declined 43 percent and 27 percent in the western and central basins of Lake Erie respectively between 1988 and 1989 (May to November periods). Preliminary results indicate a further decline in 1990, especially in the western basin. Dreissena is obviously competing successfully with filter feeders for phytoplankton. The production of faeces and psuedofaeces by Dreissena should favour other benthic organisms and early observations indicate an increase in gammarids in western basin reef areas. There is concern that a build-up of organic matter in the interstitial areas around the mussels could reduce dissolved oxygen concentrations through decomposition to the point where survival of fish eggs was adversely affected. However, a joint study with the Department of Fisheries and Oceans in April, 1990, indicated that dissolved oxygen was at or near saturation levels on walleye spawning reefs in the western basin of Lake Erie. Further studies are required to determine what happens to oxygen concentrations as organic matter and layers of mussels accumulate.

There are early indications that water taste and odour may be affected at water treatment plants (WTP) by Dreissena. Taste and odour problems occurred at the Windsor WTP in the summer of 1990 and were attributed to Dreissena either directly from the bodies of veligers and adults or indirectly from increased populations of aquatic plants because of improved water clarity. Additional research is required to delineate causes of taste and odour problems and also to determine to what extent Dreissena is improving water quality by concentrating contaminants.

CROSS-DISCIPLINARY ANALYSES OF ENVIRONMENTAL HEALTH STUDIES SUGGEST THE NEED FOR NEW APPROACHES TO RISK ASSESSMENT

by

Theo Colborn, Ph.D.
Fellow, W. Alton Jones Foundation
Senior Fellow, World Wildlife Fund/Conservation Foundation

A comprehensive examination of the literature on wildlife and human health in the Great Lakes basin provides incentive for new approaches to assess hazard from exposure to bioaccumulative, toxic substances. A review of the mechanistic actions of the contaminants commonly found in wildlife and human tissue further supports the need for change. Current public health strategies to measure population effects are too blunt to detect the subtle health decrements that may occur as a result of exposure to these chemicals. Breakthroughs in understanding the effects of a number of these persistent, pervasive organic chemicals are being made in the Great Lakes region by integrating research in wildlife, human, veterinary, and animal toxicology, ecology, epidemiology, and cellular and tissue biology. Following years of monitoring contaminants in the ecosystem, researchers in these disciplines are beginning to interpret what the concentrations mean in terms of wildlife health effects. This information provides new tools for public health authorities to assess the status of human health.

Sixteen top predator species in the Great Lakes basin have experienced severe reproductive problems accompanied by population declines since the 1950s. The health of many bird species showed marked improvements in the 1970s as the result of reductions in DDT and its metabolites producing thicker egg shells and improved reproductivity. Today, health problems that are just as serious but far more subtle than eggshell thinning are still reported in top predator species. Few overt symptoms are reported in adult animals -- instead, they are observed in offspring of exposed animals.

Health problems observed in wildlife offspring have been associated with elevated exposure to a number of contaminants. Researchers infer this exposure is the result of parental transfer through the egg, placenta, breast milk, and/or feeding of contaminated prey to offspring. Anomalies reported in wildlife offspring include: metabolic problems that cause low birth weight, loss of weight gain, and in some instances death from wasting; edema; birth defects; embryo, chick, fetus, neonate, and young adult mortality; behavioral changes; target organ damage; immune suppression; and abnormal sexual development.

An examination of the literature on the chemicals most often found in both Great Lakes wildlife and human tissues was undertaken. With one exception, (benzo a pyrene) these contaminants are not acute toxicants and genotoxicants, nor have they been determined unequivocally to be human carcinogens. They are developmental toxicants. Research at the cellular and tissue level shows that the mechanisms of action of the critical Great Lakes pollutants are often similar and general in nature. Most of the critical chemicals found in elevated concentrations in Great Lakes biota are capable of affecting normal metabolism and development in at least one or all of the following ways. First, they block cell to cell communication. Second, they induce enzymes in a number of tissues that enhance the excretion of hormones naturally produced by the endocrine system. And third, because of their chemical structure they have an estrogenic influence as well. All three mechanisms under proper timing and dose can lead to abnormal development. The cumulative effect of mixtures of these chemicals at the cell, tissue, and organ level is just beginning to be understood.

It is important to note that in laboratory animals a number of developmental health decrements have been associated with specific PCB, dioxin, and furan congeners and a number of pesticides including DDT and its metabolites, dieldrin, lindane, hexachlorobenzene, and others. These adverse health effects include wasting, edema, birth defects, immune suppression, target organ damage, effeminization of male animals, behavioral changes, and premature death, all in a dose-related manner; the same health decrements reported in Great Lakes wildlife.

Most importantly, except for a few fish species and the Beluga whale, cancer has not been reported in Great Lakes animals. Unfortunately, most risk assessments are based on cancer, not developmental effects, with the exception of mercury and lead.

A global search of the literature on residues of these contaminants in human tissues reveals they are found in all reproductive tissue, including breast milk. As a result, exposure during the embryo, fetal, and perinatal periods can be elevated on a weight to weight basis, coinciding with a period of rapid development that sets the course of development through maturity. Recent laboratory studies using a number of these chemicals revealed that obvious health effects may not be fully manifested until adulthood in exposed animals. Using wildlife and animal studies as models to assess human health, new technologies are needed to measure human exposure as well as new approaches to measure the possible cognitive, behavioral, and social effects of developmental toxicants.

C1

ENVIRONMENTAL CONCERNS - KEEPING OUR PERSPECTIVE

John P. Nunan, P.Eng., President
Trow, Dames & Moore

INTRODUCTION

This talk is intentionally provocative. The purpose of the presentation is to put before you a number of current, relatively high-profile, environmental concerns, and to discuss these in brief so as to stimulate thinking as to the type of research that might be undertaken to enhance knowledge of these issues, and putting them in truer perspective as they may affect public health and safety, and the quality of our physical environment.

Four concerns (issues) have been selected for discussion, not necessarily because of their importance, but rather due to the fact that these issues have been around for some time with little growth in our understanding of their true significance and seriousness. They are also issues that are causing much concern to various segments of the community and expenditures of large amounts of money to mitigate, possibly with less than adequate understanding as to why or if such mitigation is effective, or really required.

As Professor P.H. Jones has said, "society is engulfed in fear". This fear is not based on scientific findings, which have demonstrated that harm can result. It is based more on our ability to detect certain substances in our environment which we have discovered can adversely affect humans if ingested in large quantities. It is wrong to equate, in the minds of the public, the mere detection of a substance with ghastly public health threats. Such concerns have tremendously complicated life and in several instances have brought some forms of desirable development to a grinding halt. Some specific issues causing these concerns will now be discussed.

1) Methane Gas

Methane is a naturally occurring light hydro-carbon gas that results from the biodegradation of carbonatious material in the absence of oxygen. Methane is very widespread in nature and comprises approximately 95 percent of natural gas. Methane is produced in significant quantities during anaerobic decomposition of solid wastes in garbage dumps. It is also produced in earth fills where relatively small quantities of biodegradable material such as grass, brush and swamp debris has been incorporated in the fill. Methane can migrate from its location of generation to accumulate in buildings and other works where ignition of the gas has resulted in destruction of buildings and loss of life.

Today, the measure of a methane hazard or risk is usually determined by the insitu concentration of the gas. Is this appropriate? Is there a better way to evaluate the hazard? Is it really necessary to restrict development as much as we now do because of the presence of high insitu concentrations of methane? Are there, or can there be developed reliable methods of measuring methane flux directly, which, when compared to conservative estimates of building ventilation, will show when a buildup of methane is so improbable that development of a particular site should not be constrained?

The issue of methane recovery from large, or even small garbage dumps, seems to offer a potentially attractive opportunity for energy recovery. This is already being achieved at some very large landfills, where the cost of energy is high and a suitable market for that energy is available. Some of the questions that need to be answered through research include: What are the conditions that enhance the rate of methane production? Is it better to keep landfill dry so as to restrict the rate of methane production, which also delays stabilization of the landfill, or is it preferable to develop sanitary landfills so as to enhance methane production? How would the recovery and use of methane from a landfill, where methane production was intentionally enhanced, compare economically with other forms of waste recycling for energy, conservation and recovery, such as the burning of refuse-derived fuel from waste? What do we know about the character of the solid waste that goes into our Canadian landfills? Are we perhaps missing opportunities or even aggravating conditions by some current practices such as removal of materials from waste streams that would produce methane, when the cost of reusing these materials in other ways is less attractive?

2) Nitrates In Groundwater

Nitrate which is an essential compound for plant growth and which is naturally produced in the environment by bacterial activity and to a much smaller degree, by electrical storms in the atmosphere, has become a major concern relative to the potable use of groundwater. The use of nitrate in fertilizers to increase food crop yields in rural areas and the heavy use of nitrogen fertilizers to grow green lawns in urban areas is increasingly suspected as being the cause of nitrate buildup in groundwater, which in many areas has risen to fifty percent, or more, of the accepted 10 ppm for drinking water. This change has caused concern that the trend will continue, which in turn has resulted in rejection of some well supplies intended for municipal use, even though all other quality and quantity factors are favourable. The limit of 10 ppm has been conservatively accepted as a safe limit for consumption by infants who are more susceptible to nitrates than are older children and adults. A question we should perhaps ask is: should these sources of water supply be rejected because of an increasing nitrate trend, when the content is still well below the accepted health standard? Does the trend mean that the nitrates will in fact rise above the limit? It can be shown that the use of fertilizer for cash crops will theoretically increase nitrates in groundwater over broad areas of intensively cultivated land by as much as five parts per million, but that level should not rise much higher under prevailing climatic conditions. The level of nitrate in water at a specific sampling point may not establish the content in the water from a heavily pumped well that draws water from a broad area of one or two square miles. Do we really know at what level nitrates significantly affect the health of humans? Can we demonstrate by research how significantly agricultural fertilizer affects groundwater quality? Are we rejecting plentiful supplies of water because of concerns over nitrate buildup and trace amounts of other agricultural chemicals where detailed study may show that this is unnecessary?

3) Landfill Leachate

Leachate is produced in landfills when precipitation percolates through buried solid waste, when waste is deposited below the water table, or when the water table rises into waste because a thick pile of slowly permeable waste alters the local hydrologic regime. Dissolved in landfill leachate are constituents of virtually everything that is in the waste itself and indeed some compounds that are produced by the mixing and interaction of solutes from waste. Leachate is for the most part, produced under anaerobic conditions and has a putrid odour. Because leachate contains many known, and suspected but unknown, water pollutants, great emphasis has been placed recently on the containment of landfill leachate by lining garbage dumps, and attempting with no proven success to cover them so as to restrict infiltration of precipitation. Recognizing that leachate accumulates, it is drawn off and disposed of in waste water treatment plants. Unfortunately, very little hard data exist on how effectively leachate is renovated by conventional secondary waste water practices. We know that BOD is reduced. We know that VOCs are removed; but to where, to the atmosphere? What is the fate of soluble inorganics? They are undoubtedly diluted before release to surface streams, but do they still persist to impact surface water?

Is secondary waste water treatment really superior to the attenuation treatment and dilution that takes place naturally in the soil beneath and around landfills as the leachate is carried slowly by groundwater? We know from experience that leachate contaminated groundwater beneath some very large landfills is renovated by natural processes within a few hundred metres of the landfill. Is this a legitimate use of a small segment of the natural environment? We know the effect will not be permanent. Have we made any quantitative studies to compare the effectiveness of natural subsurface treatment with conventional waste water treatment practices? What are the cost implications? Are we creating problems by making our waste dumps too large? Do we in fact know how seriously leachate affects health? Are there any authentically documented cases to show that waste residues in groundwater affected by landfills have actually made people sick? What evidence have we that artificial containment systems actually stop leachate escape permanently?

In summary, are garbage dumps the alleged monstrous insult to the environment they are thought by many to be, or do they indeed represent a legitimate, temporary use of very small segments of the physical environment? The actual land area used for sanitary landfill is relatively small in spite of the popular contention that we are burying ourselves in our own waste. Have you ever, on a clear day flying for one hour between Montreal and Toronto tried to locate the sanitary landfills? It is difficult, because they are on that scale very small and far between. If we attempted to prove that landfills are a legitimate land use rather than to look microscopically at their adverse effects, might we discover something useful?

4) Soil Classification Criteria For Landfills

In Ontario, disposal criteria have been developed which are designed to control the chemical quality of contaminated soil that, under Ontario Regulation 309 and the Decommissioning Guidelines, must be removed from decommissioned sites. Unfortunately, these rigourous criteria have caused a lot of inert material to be diverted to expensive and already severely burdened sanitary landfills, when much of the material would be perfectly safe if left where it was, or used to "make ground" for useful development. If the soils are classified as registerable waste or subject waste, the transportation and disposal cost in the Toronto region may range from $80.00 to $250.00 per tonne, depending upon the haul distance and character of the material.

The definition of inert fill is so broad that what constitutes inert is often a matter of opinion. Operators of "clean fill" sites are frequently unwilling to accept material if there is doubt as to its origin or chemical content. As a result, sites for disposal of marginally contaminated soil are very scarce.

Prior to acceptance by a municipal landfill, chemically contaminated soil of the type described above must be classified according to Ontario Regulation 309. The Regulation 309 classification procedure involves an acid leach test and comparison with criteria set out in Schedule 4 of the Regulation. Soils that leach less than 100 times (X) the Schedule 4 criteria are acceptable at a municipal landfill subject to further classification as to whether the soil is non-registerable (<10X the criteria), registerable (10 to 100X the criteria) or inflammable.

In my opinion, key questions that need to be addressed; particularly, for soils that are classified as non-registerable are: Is disposal of such soils at a municipal landfill responsible management of scarce landfill capacity? Certainly, in the Toronto area this is a valid question; particularly, when such soil has not generally been utilized for daily cover but rather incorporated into the waste cells? A possible answer may be that in the short term, revenue from receipt of materials classified as waste is considerably higher than materials received for top cover.

Is the current Regulation 309 leachate extraction procedure a proper method of evaluating disposal options for marginally contaminated soils in southern Ontario where conditions are naturally alkaline and where mono disposal of such soils would seem to be the preferred and most cost effective disposal option?

C10 Oxidation to Remove Trichloroethylene from Soil;
G. Farquhar, University of Waterloo, Waterloo, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

D1

ION MOBILITY SPECTROMETRY IN ATMOSPHERIC ENVIRONMENTAL MONITORING IN THE US SPACE PROGRAM, G.A. Eiceman, Department of Chemistry, New Mexico State University, Las Cruces, NM 80003

ABSTRACT

The utilization of chemical instrumentation, originating with military establishments, for monitoring atmospheric environmental quality in domestic and space applications represent a little known and potentially rewarding example of technology transfer. Human exposure to hazardous airborne organic vapors at trace levels presents challenges in areas of risk assessment, toxicology, and technology of chemical sensing. Since ca. 1965, improvements in laboratory tools for measuring contamination have kindled interest in health effects from exposures that previously were disregarded. Still, refinements in toxicology, risk assessment, and human protection in those instances were dangers are certain have been hindered by limitations in chemical analysis of environmental and biological samples. While extraordinarily advanced tools for chemical characterization of samples are available, the expense and associated mechanical or electrical requirements of such instruments preclude uses in routine or continuous manner. As a result, the philosophy of environmental analysis has remained stagnant for the last two decades in spite of impressive sophistication of chemical instrumentation. A shift toward continuous monitoring or at least small portable chemical instrumentation is necessary and has been hindered only by the inherent properties and behavior of available technologies for chemical sensing.

Ion mobility spectrometry (IMS) is a derivative technology of a family of ionization detector based upon the conversion of hazardous vapors to ions in air at atmospheric pressure. In IMS, the ions are largely intact, though ionized, molecular species that can be analyzed for speed of movement in a weak electric field. This speed or ion mobility provides a measure of individual chemical constituents through the relationship of size-to-charge rather than mass-to-charge used throughout mass spectrometry. Thus, IMS can be viewed as an advanced smoke alarm where the ionization of atmospheric contaminants is followed by a rapid determination of the physical or chemical characteristics of the same ions. Advantages to IMS, in principal, include small size, low power, and trace detection limits but these were not realized until 1985.

Early developments of modern IMS can be dated to ca. 1965 when a military contract resulted in prototype hardware designs. Commercial versions were publicized in 1970 and several research groups, each with a particular developmental or investigative emphasis. Despite the demonstrated favorable response of IMS toward an impressive range of chemical classes, IMS was regarded widely as potentially significant but with serious limitations in selectivity and reliability. Studies during the last decade have shown these reservations to be rooted in the particulars of mechanisms of ion formation at atmospheric pressure rather than in ion mobility measurements.

Extensive in the consideration of IMS for environmental monitoring was the decision by the US and UK defense establishments to refine IMS for chemical warfare agent detection on battlefields. Ramifications in the use of instrumentation, formerly considered delicate and cumbersome, in such a hostile environmental included rugged, simple, and hand-held designs with refined ionization chemistry for integrity of response. In short, IMS was converted from a laboratory tool to a field monitor in a manner unlike any previous chemical analyzer. Present estimates of military distribution suggest an expansive role for IMS in armies of most western governments.

Instrumentation worthy of combat environments provided an impetus to explore civilian applications and in two instances found niches in the US space program. These two applications that are currently in testing or developmental stages include screening for vapors of hydrazines in the shuttle air lock and the use of portable gas chromatography/ion mobility spectrometry (GC/IMS) as a total hydrocarbon monitor for ambient air. In each instance, a fundamental obstacle to the utilization of IMS as envisioned and the primary emphasis of our research program has been the description and refinement of the chemistry of ionization. These will be discussed as used for the effective transfer of military IMS to environmental monitoring.

E1 **Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market;** B. Hull, The Conference Board of Canada, Ottawa, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

F1

UTILIZATION OF ENVIRONMENTAL RESEARCH TO CONTROL LEAD CONTAMINATION

by

Bobby G. Wixson
Dean, College of Science
Clemson University
Clemson, South Carolina
U.S.A.

ABSTRACT

Due to the lack of well founded guidelines in the United States and other countries for lead contamination in soil, a special Society for Environmental Geochemistry and Health (SEGH) task force was formed to utilize research data and actual case studies to develop a report on recommended guidelines for Lead in Soil. An action oriented plan on how to systematically evaluate lead contamination for the protection of public health or determine lead levels to be used for remedial actions will be presented with examples of how to determine action levels for control or remedial measures associated with lead contamination problems.

INTRODUCTION

Technology transfer is a scientific terminology that implies many different interpretations dependent upon how it is used. In the United States, the Federal Technology Transfer Act (FTTA) of 1986 was passed to help remove perceived barriers for collaboration and utilization of research between the public-private sector. The preamble to the FTTA bill also noted that "many new discoveries in science occur at universities and federal laboratories while the application of this knowledge depends upon industry." (Nichols, 1990). However, technology transfer is often easier to propose than to implement due to the following constraints:

1. Cultural resistance encountered within countries and specific locations.
2. Time requirements before profit payback.
3. Necessity to also transfer appropriate training to carry out new technology.
4. Uncertainties of legal or regulatory requirements.

Our present time of environmental awareness has received further intensification by current environmental crises (such as the Alaskan oil spill, etc.), so that the public demands a more rapid transition of environmental research methodologies into practical applications. One major difficulty is how to evaluate research and transfer selected laboratory or field methodologies as rapidly as possible into a new or improved technology. For example, in Canada, the proposed process of converting sewage sludge into fuel, has the potential of replacing over 700,000 barrels of oil at a possible savings of over $28 Million at present oil prices which may continue to increase in the present unstable geopolitical mideast crisis (Nichols, 1990). While this may serve as a good model to illustrate technology transfer, industry is often reluctant to invest in many processes because of the difficulty in receiving government approval for the technology proposed. Environmental research may also be utilized for the development of guidelines such as the control of lead contamination and allow for the use of appropriate technology, including remedial actions, to be approved by public health officials and regulatory agencies for use by concerned industries.

USE OF ENVIRONMENTAL RESEARCH

The absence of scientifically recognized guidelines in the United States, as well as other countries, concerning the acceptable concentration of lead in soil (Davies and Wixson, 1987) has contributed to confusion by regulatory agencies, industries, public health officials, the medical community and concerned citizens (Lead in Soil, 1988). The questions most often asked focus on possible adverse health effects and risks from lead exposure or the recommended permissible soil lead concentration to be used for remedial action at contaminated or hazardous waste sites (Davies and Wixson, 1986).

Preventive measures or control technologies are usually not applied when there is an uncertainty of regulatory requirements. Therefore, environmental research data from around the world was utilized by a Society for Environmental Geochemistry and Health (SEGH) task force in developing a report on recommended guidelines for "Lead in Soil" (Wixson, 1988). This report illustrates how cooperative efforts between industries and regulatory officials may be applied to determine the risk of human exposure to lead (Davies and Wixson, 1989). The methodology used in this report also shows how environmental research can be applied to develop guidelines necessary for the application or control of remedial technologies.

The SEGH task force was formed in 1988 to address the problems, evaluate data and develop scientific recommendations concerning lead in soil. The risk assessment steps of: 1) hazard identification; 2) dose-response assessment; 3) exposure assessment; and 4) risk characterization were used develop a "Phased Action Plan" (illustrated in Figure 1) which evaluates the relationship between blood lead levels and the levels of lead in soil as one possible source of exposure. The "Phased Action Plan" also required extensive review of research data and case studies for the development of a target soil lead/dust lead guideline model derived from the use of documented health criteria.

The factors associated with Lead and Health are concerned with the population groups at risk from the possible adverse health

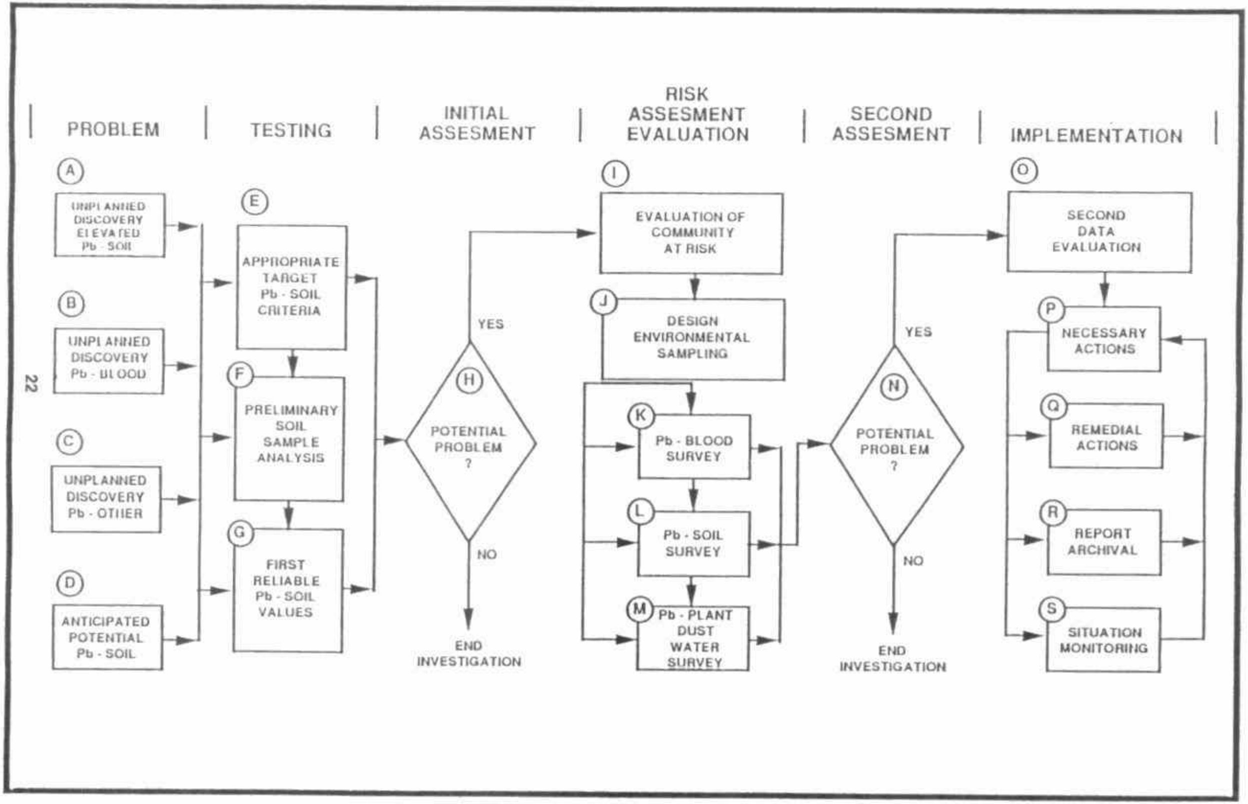
PROBLEM
TESTING
INITIAL ASSESMENT
RISK ASSESMENT EVALUATION
SECOND ASSESMENT
IMPLEMENTATION
A
UNPLANNED DISCOVERY ELEVATED Pb - SOIL
B
UNPLANNED DISCOVERY Pb - BLOOD
C
UNPLANNED DISCOVERY Pb - OTHER
D
ANTICIPATED POTENTIAL Pb - SOIL
E
APPROPRIATE TARGET Pb - SOIL CRITERIA
F
PRELIMINARY SOIL SAMPLE ANALYSIS
G
FIRST RELIABLE Pb - SOIL VALUES
H
POTENTIAL PROBLEM ?
YES
NO
END INVESTIGATION
I
EVALUATION OF COMMUNITY AT RISK
J
DESIGN ENVIRONMENTAL SAMPLING
K
Pb - BLOOD SURVEY
L
Pb - SOIL SURVEY
M
Pb - PLANT DUST WATER SURVEY
N
POTENTIAL PROBLEM ?
YES
NO
END INVESTIGATION
O
SECOND DATA EVALUATION
P
NECESSARY ACTIONS
Q
REMEDIAL ACTIONS
R
REPORT ARCHIVAL
S
SITUATION MONITORING

Figure 1. Phased action plan for lead in soil

effects of lead. Therefore, health criteria and research data were used in deriving a target soil/dust lead guideline concentration.

A single number for a lead in soil guideline for the protection of young children was considered unrealistic for a number of reasons. The population at risk can itself vary; therefore, the soil/dust guideline was established as a relationship or formula, in order to allow for a variety of environmental situations and regulatory criteria.

In the model developed, blood lead concentration was equated to a baseline level plus an increment resulting from exposure to soil or dust lead. The model also takes account of the chosen blood lead guideline or target concentration and the degree of protection requred for the population. The slope of the blood lead-soil lead relationship is then used in calculating an increase in blood lead over a baseline value. Hence the soil guideline, can vary depending on a variety of factors, allowing this response to be adjusted for a given situation with the opportunity of being modified as more research data become available.

The derivation of the blood lead/soil lead model is illustrated in Figure 2.

The major uncertainty in the use of such a realtionship is the value to use for δ , the response of blood lead to increasing soil or dust lead concentration. It therefore appears that a value in the range of 2-5 would be appropriate for most siutations and that the major influence on a value for δ may in fact be child activity rather than any characteristics of dust or soil.

RISK MANAGEMENT

The risk management section of the SEGH report emphasizes the exposure assessment and development of a relationship between blood lead levels and the concentration of lead in soil to formulate suggested guidance for acceptable soil lead. Geographic and physical processes that affect soil lead accumulation are discussed along with social aspects of lead contamination and other risks.

Legal aspects and cleanup levels for lead are presented along with economic considerations of appropriate technology utilized for remedial actions.

SUMMARY

The lack of guidelines or regulations often contribute to difficulties in implementation of improved technology for the control of metal contamination. The use of environmental and human health research data coupled with case studies of lead contamination have been used by a SEGH task force to develop a

TARGET SOIL/DUST LEAD GUIDELINE MODEL DERIVED FROM USE OF HEALTH CRITERIA

$$S = \frac{\left| \frac{T}{G^{n}} - B \right|}{\delta} \cdot 1000$$

where:

S is the soil or dust guideline, a geometric mean concentration in µg Pb per gram of dust (ppm)

T is the blood lead guideline or target concentration, in µg Pb/dl whole blood

G is the geometric standard deviation of the blood lead distribution, typically in the range of 1.3 to 1.5

B is the background or baseline blood lead concentration in the population from sources other than soil and dust

n is the number of standard deviations corresponding to the degree of protection required for the population at risk, and would normally follow from the way in which the blood lead guideline T was defined

δ is the slope or response of the blood lead - soil(dust) lead relationship and has the units of µg Pb/dl blood increase per 1000 ppm increment of soil or dust lead

Figure 2.

Derivation of the blood lead/soil lead model report on recommended guidelines for lead in soil. These guidelines are necessary to control of lead contamination by recommending action levels to protect public health. Recommended levels of lead contamination in soil also may be used to determine how clean is clean? when remedial action is necessary.

ACKNOWLEDGEMENTS

The support of the Society for Environmental Geochemistry and Health, the International Lead Zinc Research Organization, Inc., the Lead Industries Association and the US Environmental Protection Agency is acknowledged. Special thanks also to the members of the Lead in Soil task force for their time and effort on this important project.

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VOLUME I

PANEL PRESENTATIONS

P1

"GLOBAL WARMING: WHAT IS AT STAKE?

THE INTERNATIONAL SCENE: J. P. Bruce

With the first assessment report of the Intergovernmental Panel on Climate Change (IPCC), and the Second World Climate Conference (SWCC) completed, discussion of greenhouse gases and climate change are now moving to a more formal stage of international negotiation of a Convention on Climate Change. The positions taken by various countries at the IPCC meetings and the debates at the SWCC give clear indications of some of the major issues that will have to be addressed in negotiation of a global Convention. These issues will be identified and some possible means will be suggested of addressing the diverse concerns.

Major changes in both environmental and economic policies, especially in the energy sector, will be needed in most countries if an effective international agreement is to be reached.

P2

GLOBAL WARMING: A CANADIAN PERSPECTIVE AND ACTION STRATEGY

Dr. D. Kirk Dawson
Director General
Canadian Climate Centre

Climate Change is perhaps one of the best examples of global interdependence of countries. An effective response will require a global effort which is likely to have considerable impact on human kind. A major dilemma, however, is that actions may be required well before many of the specific issues can be analyzed more thoroughly by further research.

Some of the more stringent actions that may be required, particularly those which serve to limit emissions of greenhouse gases, will have a profound effect on national policies in all areas. The manner in which nations address this issue will have major implications for trade and economic balance, between industrialized and developing countries, between industrialized nations themselves and within the different regions of individual countries.

Canada has played a significant role in seeking international solutions. We have been an active participant on the Intergovernmental Panel on Climate Change (IPCC) and are strong proponents of the negotiation of a comprehensive global convention on climate change.

At home, Canada supports a world-class climate research and impacts program and is now working with the provinces to conclude a National Action Strategy on climate change. The strategy will be:

- Comprehensive. It will deal with all of the major sources of greenhouse gases and the sinks of those gases;
- National in Scope. It will contain strategies appropriate for all levels of government, as well as industry and individuals, while recognizing that climate change is a global problem requiring international cooperation; and
- Action-oriented. It will be a cost effective and flexible action program that is based so that it can respond to new understanding and developments in the future.

P3

Global Warming: What Is At Stake?
Socio-economics

Erik Haites

In relation to global warming, socio-economics could cover many issues. To meet my time constraints, I must limit the scope of my presentation.

I will not discuss the socio-economic consequences of global warming, nor the socio-economic implications of adaptation to climate change. For Ontario, these were reviewed at a workshop organized by the A.E.S. in November 1985. A summary of that workshop is available in the Climate Change Digest (CCD 88-08) "CO_2 Induced Climate Change in Ontario: Interdependencies and Resource Strategies."

Today, I will focus on two socio-economic aspects of global warming that are the subject of more current research. They are:

- the costs of achieving reductions in emissions of greenhouse gases, and
- the potential application of economic instruments to reduce greenhouse gas emissions.

Following the Toronto Climate Conference in June 1988, analysts started to examine how the proposed interim target of a 20% reduction in 1988 emissions of CO_2 by 2005 could be achieved. I reported on such an analysis for Canada at this conference last year. During 1989 and early 1990, studies were completed for a number of countries. The universal conclusion is that the Toronto Conference target is a tough one. Virtually, all currently available CO_2 emissions abatement measures will need to be implemented to their full technical potential to reach that goal.

Once the measures needed to achieve the target are known, people want to know the cost of implementing those measures. Although some preliminary answers are available, this is a matter that is currently under intense study.

The preliminary cost estimates range from about -0.3 to +0.5 percent of GNP annually to 2005. Some studies show net savings, as a result of lower energy consumption, from measures to reduce emissions of CO_2. Other studies show a net cost for these measures. The results tend to vary systematically with the methodology used.

Typically, energy efficiency, measures account for the bulk of the CO_2 emissions reductions to 2005. Studies that analyse the economics of individual energy efficiency measures, find most of these measures to be attractive from a societal perspective. They assume that the measures are implemented as part of the normal replacement cycle. This yields an overall saving as a result of implementing the CO_2 emissions reduction measures. Studies for Canada and Australia are good examples of this approach.

The other approach to estimating the cost of CO_2 emissions abatement is to use a macro-economic model. A carbon tax is used to achieve the target reduction in emissions. The tax revenues are recycled so that there is no net loss to the economy. Studies of this sort for the U.S., Japan, and other countries, all yield positive costs for CO_2 emissions reduction.

The carbon tax approach causes all energy users to adjust their energy consumption and equipment at the same time, reflecting the introduction of the tax. Adjustments do not reflect the replacement cycle for energy using equipment, thus raising the adjustment costs. On the other hand, assuming that all adjustments occur as part of the normal replacement cycle and that the adjustment costs of the equipment producing industries are reflected in the equipment prices, undoubtedly understates the adjustments. There are probably other reasons as well for the differences in the cost estimates produced by the two methodologies.

In any event, the first order estimates of the cost are between -0.3 and +0.5 percent of GNP. Research currently underway will refine these estimates and provide a better understanding of the nature and magnitude of the costs.

Economists believe that policies, such as emissions charges or tradeable emissions permits, can achieve a specified environmental target at lower overall cost than emissions regulations. Given the scale of the emissions reductions proposed by the Toronto Conference target, cost-effective policies are doubly important. I stressed the need for such policies in last year's session.

Tom Tietenberg and I have outlined a linked system of emissions permits and emissions taxes for carbon dioxide and other greenhouse gases. Briefly, the system is as follows. Each country is assigned emissions targets by international agreement; developing countries would probably have targets greater than current emissions and developed countries might have targets 25 percent below current emissions.

Within a country, such as Canada, large sources could earn permits for reductions beyond their target. Other large sources, such as industries, electric utilities, and large commercial and institutional facilities, could purchase permits in order to reach their target reduction. The fuels used by smaller sources, residences, vehicles, and small commercial facilities, would include an emissions tax equal to the market price of the permits. Thus, all sources have the same target reduction and the same cost per unit of CO_2 reduced.

International trade in permits would be allowed. However, each country could establish import and export restrictions. Developing countries could restrict trades between subsidiaries and parent companies if they chose. A country could restrict imports from countries whose permits it judged to be of dubious value. These arrangements provide economic incentives to participate in the international agreements for control of greenhouse gases. And, they provide enforcement mechanisms without requiring an international inspectorate.

The system, we believe, could be extended to CFCs, many sources of methane emissions and afforestation, but not to nitrous oxide, ozone, or ground level ozone precursors.

In conclusion, policy analysis of global warming is proceeding at a very rapid pace. Last year, the potential abatement measures and the scale of the response required were just being determined. They are now fairly well known and preliminary estimates of the associated costs are available. These cost estimates are being refined and appropriate policies are being formulated. Next year, I hope that we will know what policies are to be implemented in Ontario, in Canada, and internationally.

P4

WARMING TO A CRISIS:
THE MEDIA AND CLIMATE CHANGE

Abstract for a speech

By Michael Keating
Environment Writer and Consultant

to

The Technology Transfer Conference of Environment Ontario
Royal York Hotel
November 20, 1990

Global warming hit the front pages in Canada in October, 1983. This came immediately after the New York Times broke the story of the EPA report by John Hoffman, saying the greenhouse effect would begin in the 1990s.

This led to a small flurry of stories, which grew slowly but steadily into a trickle, and, over the last few years, into a flood.

The pace of coverage picked up in the mid-1980s as more of the big media, such as Time Magazine and the TV networks, caught on to climate change as a mega-story. There was talk of a threat to human life.

It was and is a great story for graphic images. Belching smokestacks and burning forests. Kentucky winters in Toronto. Glaciers crashing into the sea as the ice caps melt. Waves lapping at the doors of Wall Street. Two, three or four Prince Edward Islands. Florida going back the the alligators. Hurricanes with 40 to 50 per cent more punch than now.

People even coined the term "heat beat" for reporting on climate change.

The story got a real boost in 1988 when reporters had both the devastating heat waves in central North America and the Toronto conference on the changing atmosphere. And that was when James Hansen of NASA told the U.S. Congress that he was 99 per cent sure that climate change had begun.

The seriousness of the issue was reinforced by the record drop in the Mississippi River and ensuing calls from some U.S. politicians for water diversions from the Great Lakes.

So, how have the media covered the science of global warming?

Since the early 1980s, reporters have generally accepted that climate change is a real and poses a serious threat. They have given relatively little coverage to scientists, or politicians, who say this is just a theory.

I think reporters feel global warming is a fairly easy concept to grasp. Humans put billions of tonnes of gases into the atmosphere. Billions is a big number, so it must have an impact.

Reporters have generally treated climate change as a "bad thing" but that has not been universal. There are still some stories about the benefits of warmer winters and less snow.

How responsible have the news media been in reporting on global warming? By and large the reporting that I have seen has been fairly accurate. It has been much better than coverage of some issues such as PCBs.

But whether or not you like the coverage so far depends a lot on what hat you are wearing.

If you are a scientist who believes that global warming is a problem, then you are probably happy with the fact the media have made the greenhouse effect as common a phrase as acid rain. I think the environment movement feels the same way.

If you are a scientist who believes it is just a theory, then you probably feel the media have not been critical enough of the other scientific camp.

If you a minister of environment and have been in the portfolio long enough to understand the issues, then you probably like the coverage. You will hope that the media put more pressure on the premier or prime minister and the minister of energy to come up with greenhouse gas strategies.

If you are the minister of energy you probably wish the media would stick to covering the deficit or the ups and downs of the stock market.

If you work for the oil and coal industry you probably don't want to open your paper in the morning.

Where will news coverage go in the future?

The media are on to the fact that, per capita, Canadians are the world's greatest energy users and one of the world's greatest producers of greenhouse gases.

Where will the mud from this kind of coverage stick?

That's very hard to predict. A lot depends on the critics and on scientific research that is released to the public.

We have already seen considerable criticism of the coal-burning power plant at Point Aconi, Cape Breton, and some criticism of Hibernia in the east, and heavy oil projects in the north, because of they will all add CO_2 to the atmosphere.

There is an increasing number of stories about CO_2 from automobiles but the media have an ambivalent role in this one, since most reporters drive cars, and the media get a lot of revenue from auto ads.

The media face at least two difficult tasks ahead.

One will be in deciding when to report that global warming has started. The second will be in focussing on what to do about the problems.

Expert groups, including the Toronto atmosphere conference, suggested that the world should start switching to low or no carbon fuels such as hydro-electricity, wind, solar power, natural gas, biomass and possibly nuclear energy, if it can be made safe and if its use does not lead to more nuclear weapons.

We are also hearing calls from less developed nations for massive assistance to help them cut or avoid the emission of greenhouse gases while reducing poverty, hunger and disease.

These are complex stories, often without a clear set of targets to shoot at. Reporters are going to need lots of help from the scientists, policy makers, researchers, environment groups and others.

I remember quoting the Brundtland Report as saying we need lifestyles that are, "within the planet's ecological means." And I remember asking Maurice Strong if humans can make that kind of shift quickly enough. He said, "it is going to be a race between our sense of survival and our more indulgent drives."

What we need now is articulate spokespersons who will tell the public, through the media, how we are going to win that race.

* * *

P5

1990 TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 20, 1990

ABSTRACT OF J.D. McFARLAND'S REMARKS

The potential for global warming has become one of the most complex and hotly-debated issues in the energy/environment dialogue. Although there appears to be an emerging scientific consensus that an enhanced greenhouse effect is real, many uncertainties remain with regard to the magnitude, timing and regional effects. Canadians as yet do not fully understand the implications of this issue on public policy development nor the economic consequences of potential policy measures to address it. The energy industry is vitally concerned about promoting sound public policy in this area, and Imperial Oil has been active in providing a perspective on the issue in the context of domestic and international energy use. Imperial's initiatives to generate a broader understanding of the scientific and economic implications for Canada and Imperial are discussed.

J.D. McFarland/wl
October 5, 1990

P6

Global Warming: What's Known and What's Not?

Bunli Yang

Global warming and what industrialized societies might do about it have become topics of intense debate. Apart from its importance as an environmental issue, and it is often regarded the most serious threat to the global environment, global warming has many uncertainties. That kind of uncertainty generates debate and may be a barrier to action.

It is straightforward to list what is known about global warming and climate change:

- there is a natural greenhouse effect in our atmosphere because of gases that trap heat;
- the natural greenhouse effect accounts for a warming of about 33 C.;
- the climate of an ice age differed from today's by a small change in average temperature, about 5 C.;
- in the past, average temperatures and concentrations of the greenhouse gases have been high together and low together;
- human activities have been increasing the concentrations of the greenhouse gases in the atmosphere;
- the impacts on climate of rapid changes in temperature will not be uniform;
- climate is inherently global, and international agreement on actions will be very difficult.

The list of unknowns is, of course, endless. They range from the phsyical science of clouds and oceans to the economics and the social impacts of climate change. Examples are the rise in sea level for any level of greenhouse gas concentrations, or the rate of temperature rise, or the amount of precipitation and soil dryness because of any warming, or the costs of prevention, or the costs of adaptation to climate change. The risks of climate change, though not known or even knowable, are widely regarded to be major.

While these unknowns may loom large, uncertainties about usual economic trends are even larger, but are not barriers to economic policies and actions.

For purposes of public policy, the relevant question is not "How much needs to be known with high certainty before taking action?" but "**What should be done now, by whom, in the face of the risks**?"

VOLUME I

SESSION A

AIR QUALITY RESEARCH

VERBAL PRESENTATIONS

A2

Genetic Characteristics of Healthy and Declining Sugar Maple (*Acer saccharum* Marsh.) in Ontario

P. Knowles and D.J. Perry

School of Forestry/Department of Biology
Lakehead University
Thunder Bay, Ontario
P7B 5E1

Over the past few years forest decline has attracted global concern (Schutt and Cowling, 1985; Knight, 1987) with the changing chemical climate proposed as a probable contributing factor (Anderson, 1989; Schulze, 1989) in combination with an interaction of other stress factors. Among Canadian species, sugar maple (*Acer saccharum* Marsh.) has elicited the greatest concern with reports of decline in Ontario as early as 1947 (McIlveen *et al.*, 1986). Causal factors remain obscure with indications suggesting that acidic precipitation as but one more stress in addition to those of insect outbreaks and drought (Hendershot and Jones, 1989; Linzon, 1986; McLaughlin *et al.*, 1985).

Previous research in pollution and forest trees has provided reason to believe that genetic differences may exist between healthy and declining individuals (*e.g.*, Kriebel and Leben, 1981; Scholz and Venne, 1989). Thus, concern about the potential erosion of genetic resources through the elimination of sensitive individuals has been expressed (Karnosky *et al.*, 1989; Scholz, 1981). The purpose of the present study was to determine whether possible genetic differences between healthy and declining sugar maple within the same sites are discenable at the allozyme level. Regardless of the specific causal agents, the determination of any link between genetic markers and visible injury could provide a foundation for selection and management decisions.

MATERIALS AND METHODS

Four sites previously selected as part of the Ministry of the Environment studies (Beak Consultants Ltd., 1989) were chosen with two near Dorset, Ontario (named Boothby and L.M. Frost) and two near Peterborough, Ontario (called Brackenridge and Davies). At each site bud tissue was collected from each of 24 trees previously classed as healthy and about 24 classed as declining, totaling to a sample size of about 48 trees per site. A decline index (DI) was available for each tree based on percentages of dead branches, chlorosis, and undersized leaves (McIlveen and McLaughlin, 1988). Bud tissue was prepared and starch gel electrophoresis was conducted as previously described (Perry and Knowles, 1989). Only variable loci (eleven in total) among nine enzyme systems were assayed as follows: aspartate aminotransferase (*Aat*), aldolase (*Ald*), diaphorase (*Dia*), leucine-amino-peptidase (*Lap*), malate dehydrogenase (*Mdh*), 6-phosphogluconic dehydrogenase (*6pg*), phosphoglucose isomerase (*Pgi*), phosphoglucomutase (*Pgm*), superoxide dismutase (*Sod*).

Allele frequencies were estimated for both subsamples of each population based on observed genotypic arrays and allelic heterogeneity was assessed using standard non-parametric chi-square tests. Due to overlap of DI scores within some sites, healthy and declining subsamples were defined as the trees with the lowest 20 and highest 20 DI scores within each site when scores were ordered sequentially within site.

Expected heterozygosities (H_e) were estimated for each locus within each subsample as:

$$H_e = 1 - \Sigma p_i^2,$$

where p_i was the estimated frequency of the *i*th allele at the locus. A measure of the deviation of observed heterozygote frequency from that expected under Hardy-Weinberg equilibrium, F_{IS}, was calculated for each subsample as:

$$F_{IS} = 1 - H_o/H_e,$$

where H_o was the observed proportion of heterozygotes. The contribution of each locus to a subsample's mean F_{IS} was weighted by its expected heterozygosity in that subsample. Values of F_{IS} greater than 0 indicate an excess of homozygous genotypes relative to Hardy-Weinberg expectations while negative values are indicative of an excess of heterozygotes. For each site subsample differences in means of H_e, H_o, and F_{IS} were evaluated using paired *t*-tests.

The possibility of a relationship between heterozygosity and vigour was explored through a regression analysis of individual tree data. The independent variable was the proportion of loci heterozygous in a tree and the dependent variable was the tree's DI. This analysis was performed for each site using the computer program MCREG of BIOSTAT I (Pimentel and Smith, 1985).

RESULTS

Observed allele frequencies of the healthy and declining subsamples within the four sites are presented in Table 1. Allelic heterogeneity tests indicated significance (*P*=0.04) at *Mdh-3* in

TABLE 1. ALLELE FREQUENCIES OF HEALTHY (H) AND DECLINING (D) SUGAR MAPLE AT FOUR SITES (ORIGINAL DATA).

		SITE[1]							
		BOTH		BRAK		DAV		LMF	
LOCUS	ALLELE	H	D	H	D	H	D	H	D
Aat-1	1	0.98	0.94	0.96	0.96	1.00	0.92	1.00	0.96
	2	0.02	0.02	0.04	0.04	0.00	0.06	0.00	0.02
	3	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.02
	4	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Aat-2	1	0.69	0.85	0.63	0.73	0.90	0.79	0.79	0.83
	2	0.31	0.15	0.31	0.25	0.08	0.21	0.21	0.17
	3	0.00	0.00	0.06	0.02	0.02	0.00	0.00	0.00
Ald-3	1	0.90	0.89	0.98	0.90	1.00	0.92	0.90	0.94
	2	0.10	0.09	0.02	0.10	0.00	0.08	0.08	0.06
	3	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	4	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Dia-3	1	0.88	0.96	0.96	0.92	0.96	0.92	0.85	0.92
	2	0.08	0.04	0.04	0.08	0.04	0.08	0.13	0.06
	3	0.04	0.00	0.00	0.00	0.00	0.00	0.02	0.02
Lap-1	1	0.98	0.98	1.00	0.94	1.00	1.00	1.00	1.00
	2	0.02	0.02	0.00	0.06	0.00	0.00	0.00	0.00
Lap-2	1	0.96	1.00	0.98	0.98	1.00	1.00	1.00	0.98
	2	0.04	0.00	0.02	0.02	0.00	0.00	0.00	0.02
Mdh-3	1	0.92	1.00	0.94	0.96	0.98	0.85*	0.96	0.96
	2	0.08	0.00	0.06	0.04	0.02	0.15	0.04	0.02
	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
6pg-1	1	1.00	1.00	0.98	1.00	1.00	0.98	0.96	1.00
	3	0.00	0.00	0.02	0.00	0.00	0.02	0.04	0.00
Pgi-2	1	0.88	0.76	0.73	0.79	0.73	0.67	0.85	0.79
	2	0.06	0.17	0.21	0.19	0.08	0.15	0.13	0.10
	3	0.04	0.04	0.02	0.00	0.15	0.06	0.02	0.04
	4	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
	5	0.02	0.02	0.02	0.02	0.04	0.12	0.00	0.06
Pgm-1	1	0.90	0.91	0.96	0.90	0.81	0.88	0.90	0.88
	2	0.00	0.02	0.02	0.02	0.02	0.04	0.04	0.00
	3	0.10	0.07	0.02	0.08	0.17	0.08	0.06	0.12
Pgm-2	1	0.98	1.00	1.00	0.98	1.00	0.98	1.00	0.96
	2	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02
	3	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.02

[1] Site names: BOTH=Boothby; BRAK=Brackenbridge; DAV=Davies; LMF=L.M. Frost.

*Significant ($P<0.05$) difference between subsample allele frequencies within site.

Davies site only. Paired *t*-tests indicated a significant difference in the levels of expected heterozygosity of the healthy and declining subsamples within the Davies site with the declining subsample having a greater mean H_e (Table 2). However, in the remaining sites H_e was usually larger, but not significantly so, in the healthy subsamples. No significant trend was observed concerning a possible relationship between DI and observed heterozygosity and none of the sites demonstrated significant heterogeneity of mean H_o among subsamples (Table 2). A consistently greater F_{IS} was noted in the declining subsamples relative to the corresponding healthy subsamples (Table 2). Although paired *t*-tests did not find any of these observed differences within sites to be statistically significant, the apparent trend is compelling.

Not unexpectedly, the results of the regression analysis relflected the observations made of H_o above. The possibility of a relationship between heterozygosity and state of decline was strongest in the Davies site with a correlation (r) between individual heterozygosity and DI of 0.27 (P=0.06). The Boothby, Brackenridge and L.M. Frost sites had r values of -0.22 (P=0.13), -0.21 (P=0.16), and 0.05 (P=0.74) respectively. Clearly, there was no consistent trend.

TABLE 2. EXPECTED ($\underline{H_e}$) AND OBSERVED ($\underline{H_o}$) HETEROZYCOSITIES AND FIXATION INDICES ($\underline{F_{IS}}$) OF HEALTHY AND DECLINING SUGAR MAPLE AT FOUR SITES.

	HEALTHY			DECLINING		
SITE[a]	H_e	H_o	F_{IS}	H_e	H_o	F_{IS}
Both	0.18	0.19	-0.083	0.14	0.14	-0.020
Brak	0.17	0.19	-0.169	0.16	0.15	0.098
Dav	0.12	0.12	-0.008	0.19[b]	0.17	0.101
LMF	0.15	0.15	-0.028	0.15	0.15	-0.020
Pooled Data	0.16	0.17	-0.044	0.16	0.15	0.063

[a] See Table 1 for meaning of abbreviations.
[b] Estimates differ significantly ($P<0.05$) between subsamples within site.

DISCUSSION

Several observations made in the course of this study are of interest. First, where some others report increased heterozygosity in forest trees tolerant of environmental stress (Geburek *et al.*, 1987; Muller-Starck, 1985, 1989) we found no evidence of such a trend either in comparison of mean heterozygosity measures of subsamples or in the regression analyses. The only statistically significant relationship observed was contradictory with a greater mean H_e found in the declining subsample of the Davies site, but not observed in data of the other sites.

The Davies site was also unique in that significant allelic heterogeneity was observed among its subsamples for a single locus, *Mdh-3*. Such allelic heterogeneity has been observed in other studies (*e.g.*, Bergmann and Scholz, 1985) and implicated by researchers to be involved in resistance mechanisms. Since the distribution of allele 2 at *Mdh-3* in the Boothby site is opposite to that at the Davies site, we doubt that this locus is directly involved with a resistance mechanism or is a specific target of selection.

Differences in allele frequencies between tolerant and sensitive phenotypes in this and similar allozyme investigations could be accounted for by influences other than selection imposed by environmental stress. For example, the cohort structure (progeny produced during the same year) may be genetically differentiated (Mulcahy, 1975) potentially influencing the population's genetic architecture. Furthermore, differential disturbance such as soil compaction by livestock and sap collection may damage trees independent of genotype.

What inferences can be drawn from our findings? Perhaps the most notable trend observed was that of the mean F_{IS}. In spite of the fact that differences in mean F_{IS} between healthy and declining populations did not attain statistical significance, the fact that all four populations displayed greater F_{IS} in declining subsamples suggests to us that the perceived trend is something more than an ephemeral aberration. This trend indicates that the proportion of heterozygous loci per individual relative to Hardy-Weinberg expectations tends to be greater in the healthy individuals. Such a condition could occur if the more inbred individuals are predisposed to decline, or if heterozygosity in general confers resistance to decline or both. It is difficult to distinguish between these two possibilities (Mitton and Jeffers, 1989). That the significant difference in heterozygosities observed among subsamples at the Davies site had the declining subsample with the highest heterozygosity would suggest that heterozygosity *per se* does not necessarily impart resistance.

This investigation raises many new questions. Is there variation in the level of decline among cohorts within sites? What is influencing the different genetic trends among sites? For example, does the absence of a convincing genetic trend between healthy and declining subsamples among sites indicate that the allozyme procedure is inadequate or that the stresses are complex affecting trees and sites differentially? As is the case with the study of interactions of environmental stress and genetic components in general, the problems involved in the investigation of the association of genetic parameters and the maple dieback are multifarious.

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A3

Preliminary Report: Interpretation of Sugar Maple (*Acer saccharum*) Ring Chronologies from Central and Southern Ontario using a Mixed Linear Model

D.A.J. Ryan[†], O.B. Allen[†] and A.M. Gordon[‡]

[†] Department of Mathematics and Statistics
[‡] Department of Environmental Biology
University of Guelph, Guelph, Ontario N1G 2W1, Canada

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1. Introduction

Recent declines in the growth rate of tree species, such as Jeffrey pine (*Pinus jeffreyi*) (Peterson *et al.* 1987), loblolly pine (*Pinus taeda*) (Zahner *et al.* 1989), Norway spruce (*Picea abies*) (LeBlanc *et al.* 1987), red pine (*Pinus resinosa*) (LeBlanc *et al.* 1987), red spruce (*Picea rubens*) (Adams *et al.* 1985, Cook 1988, Ord and Derr 1988, Van Deusen 1987, Zedaker *et al.* 1987), Scots pine (*Pinus sylvestris*) (Kullman 1987, LeBlanc *et al.* 1987), and white oak (*Quercus alba*) (Phipps and Whiton 1987), have been extensively documented. The decline has been ascribed to such factors as atmospheric deposition, (LeBlanc *et al.* 1987, Zahner *et al.* 1988), climate changes, (Kullman 1987) and stand dynamics (LeBlanc *et al.* 1987, Van Deusen 1987).

Decline in the growth rate of Sugar Maple (*Acer saccharum*) has been reported as early as 1952 in Ontario and 1963 in Michigan (Mclaughlin *et al.* 1985). In both cases the decline was attributed to other factors such as over cutting, farming activities and heavy insect infestations. Hornbeck *et al.* (1987, as cited in Innes and Cook, 1989) suggest that in the northeast U.S. the decline associated with red pine, has not extended to the Sugar Maple. Conversely Kim (1990) suggests that Sugar maple in the Adirondack Mountains may be affected by atmospheric deposition. Recently in Ontario, observational evidence suggests that the health of larger sugar maples is deteriorating (Mclaughlin *et al.* 1985).

Statistical methods used to investigate the relationship between the decline in growth rate and various natural and anthropogenic factors are in general based on a function which removes trends associated with stand dynamics (detrending function). Such a function may be a growth curve, (Fritts 1976, Sundberg 1974, Van Deusen 1987), an empirical linear model (Van Deusen 1987), a time series model (Harvey 1984, Monserud 1986) or a digital filter (Robertson and Jozsa 1988, Craddock 1957). Upon removal of stand dynamic trends, various multiple regression techniques have been used to determine whether the remaining factors, such as climate, site suitability etc, account for a significant proportion of the variability in the standardized growth ring widths. Fritts (1976) advocates the use of principal components to summarize climatic data. Other simpler approaches utilize the monthly means and one year lagged monthly means of the climatic data.

When all natural factors have been accounted for, the tree-ring chronology is then examined for further trends which may be associated with anthropogenic factors.

Innes and Cook (1989) and Zahner *et al.* (1989) recognize that these methods may be *removing* important information pertinent to the long term trends associated with anthropogenic factors and thus may not be appropriate for investigating these relationships.

The objective of this study is to develop a statistical model which relates growth rates of sugar maples in Central and Southern Ontario to climatic and ecotypic variables. This problem is examined using a data base containing tree-ring chronologies of sugar maples from woodlots in Central and Southern Ontario, obtained from the Ontario Ministry of the Environment. The model will then be used to determine whether there is sufficient evidence to suggest that atmospheric deposition is responsible for a recently observed decline in the growth rate of sugar maple trees in Central and Southern Ontario.

These data were collected observationally. If important factors are omitted from the model, the estimates of the relationship between tree growth and the factors of interest may be biased. In situations such as this, one should be aware that alternative explanations may exist.

2. Description of Sampling Design and Data Collection

2.1 Chronology Data

The Ontario Ministry of the Environment has conducted a field trial to measure the growth rate of sugar maple and relate this to environmental conditions when the growth was taking place.

Three regions were chosen for study: Southwestern Ontario, represented by 5 plots south west of St. Williams (heavy atmospheric deposition), Central Ontario, represented by 5 plots in Barrie, and 18 plots in either the Algonquin Park and the Kawartha area (moderate atmospheric deposition), Western Central Ontario, represented by 18 plots north or east of Sault Ste. Marie (North Shore) (light atmospheric deposition).

Each plot was established using the following criteria. (1) The stand must be at least 10 ha in size. (2) It must be remote from point sources of air pollution ($\geq$ 30 km) or urban centers ($\geq$ 15 km). (3) There should be no major thinnings in last 10 years. (4) A documented stand history should exist. (5) The basal area of the plot should be between 14 and 25 m^2/ha . (6) The average age of trees should between 75 and 150 years.

Within a plot, 10 trees with a diameter greater than 10 cm at breast height were selected for sampling. When 10 trees within a plot were not available, the number of trees required to get 10 were chosen outside the plot, but as close to the plot as possible. Two of these 10 trees which were considered to be the co-dominant trees were felled for detailed stem analysis. For each tree which under went stem analysis, the specific volume increment (SVI) was then computed. This measurement is felt to more accurately represent the growth response to environmental conditions than ring widths taken from single cores at breast height.

Increment core samples were then obtained from each of the remaining 8 trees in each plot. Each tree was cored at breast height on both the north and south side of the tree. The width of each of the rings was measured and the widths of the rings from the two cores averaged.

2.2 Climate Data

Climate data were provided to the Ontario Ministry of the Environment by the Canadian Climate Center, Atmospheric Environment Service (AES). Climate data were obtained for various weather stations in the immediate area of the established plots. These chronologies were then combined to produce a complete as possible record of the climate since 1900. The following climate variables are available as monthly means: mean temperature (°C), minimum temperature (°C), maximum temperature (°C) and total rain (mm).

3. Data Analysis

3.1 Cross Correlation

Prior to investigation of an appropriate statistical model, an attempt was made to cross correlate trees within a site and between sites within an area. Reasons for this were to identify any obvious errors made in collecting, recording or transferring the data and to investigate the utility of the climate data.

3.2 Ring Widths

Cross correlation of the tree-ring chronologies was undertaken using both $R_{i,t}$, the raw ring width at time t, for the i^th tree, data and $D_{i,t}$ where $D_{i,t} = log(R_{i,t}) - log(R_{i,t-1})$. Generally when working with time series, it is desirable to work with a de-trended series. The first difference of the log (D_t) was used to remove any long term trend. This was only possible for the data from the Kawarthas, Algonquin Park and Sault Ste. Marie areas, since the data for the other sites was provided as the means on each site. However, both the raw series and a detrended series were investigated for cross correlations.

The simple correlation coefficient was calculated as a measure of the correlation between both the raw and detrended ring widths of trees within the same plot. In general the correlation between ring widths of adjacent trees was poor. A histogram of a subsample of all the correlations based upon the raw ring widths is presented in Figure 1a. Generally the correlations on the detrended ring widths were poorer.

Two possible reasons for the poor correlations are reader error and the fact that climate may not be the limiting factor for growth. The ring structure of the Sugar Maple is referred to as diffuse-porus. The structure of the cells of the early wood and late wood each season are similar, and there is little difference in the size of the cells or the thickness of the cell walls. This makes it very difficult to measure the ring widths. Thus the structure of the tree-rings could contribute to the poor correlations.

Dendroclimatology texts indicate that trees located on "good" sites generally produce complacent rings. These are rings which do not reflect yearly variations in climate, indicating that climate may not be the main factor influencing tree growth.

3.3 SVI

Attempts to cross correlate the SVI measurements met with slightly better results. A summary of the correlations based upon the raw SVI is presented in Figure 1b.

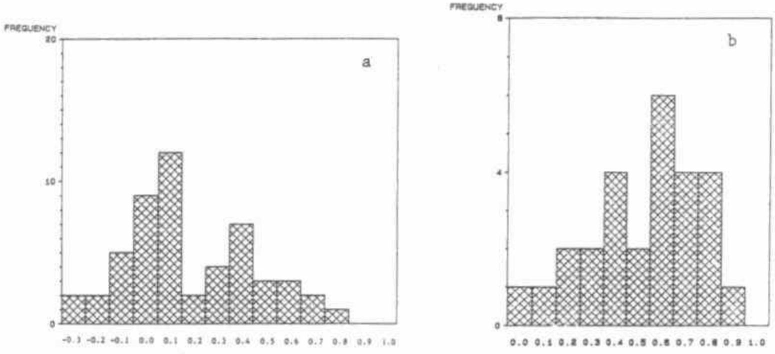

Figure 1: Histograms of the correlations between the raw ring widths (a) increments from the co-dominant trees chosen each of the plots and the raw SVI (b) increments from the co-dominant trees.

4. Proposed Tree-ring model

The model to be investigated for this study will be a general linear model treating the raw ring (raw SVI) widths as the response, and including terms for such factors as region, plot, climate, tree age, year, year by region interaction and an error. The errors associated with the rings of a tree are assumed to follow a first order autoregressive error structure. This model will regard plot as a random effect. The remaining factors and covariates will be regarded as fixed. The aggregate set of ring widths will be assumed to follow a multivariate normal distribution.

This is different from other models in the literature, since most rely on classical time series approaches, where the data is detrended prior to fitting a multiple regression model. For example, Innes and Cook (1987), Cook and Johnson (1989), and Van Deusen (1987) are examples of studies in which the ring widths are detrended using various growth curves, or low order polynomials, prior to analyzing the data. Approaching detrending in this fashion requires the assumption that the detrending curve is removing the low frequency variation associated only with the change in the growth rate of the tree related to increasing age. Zahner *et al.* (1989) uses the inverse of the age class as a regression variable to removing the low frequency variability associated with increasing age.

4.1 Autocorrelation Structure

The autocorrelation of the individual tree-ring series, will be assumed to be of first order. Thus the model becomes

$$R_t = \sum_{i=1}^{k} \beta_i x_{it} + \epsilon_t \ ,$$

where $\sum_{i=1}^{k} \beta_i x_{it}$ is the systematic portion of the model (to be discussed in the following section) and ϵ_t is the error term. Under the assumption of a first order autoregressive error structure,

$$\epsilon_t = \rho \epsilon_{t-1} + u_t \ ,$$

where u_t are assumed to be independent, normally distributed random variables with mean 0 and variance σ^2.

The method illustrated by Neter *et al.* (1983) and originally proposed by Cochrane and Orcutt (1949) will be used to estimate the first order correlation, and the estimates of the systematic component. This approach results in essentially the same analysis as suggested by Atkin (Cochrane and Orcutt 1949).

4.2 Systematic Component

4.2.1 Tree age

The volume of wood added in any given year is directly related to the age of the tree. Open canopy trees tend add decreasing amounts of wood as they age, which is characteristic of an exponential growth. Closed canopy trees on the other hand tend to follow a more complicated growth curve. This is true of the sugar maple. Thus the choice of the method for choosing a function for accounting for the geometrical constraint of adding a volume of wood to an increasing area is very important. Improperly chosen functions can either result in residuals which appear to be affected by exogenous factors or the function can remove the response of interest (Innes and Cook 1989). Both Zahner *et al.* (1989) and Innes and Cook (1989) recognize that indiscriminent detrending can obscure long term trends.

To avoid the problems induced by using a specific growth model, age related differences can removed by introducing age as a class variable in the model. The age classes are 1-5 years, 6-10 years, 11-15 years, 16-20 years, 21-30 years, 31-40 years etc. This allows the age variability to be removed, with out specifying a specific form for the growth curve. This approach has the advantage of allowing the data to specify the growth curve of the particular species, but requires that the trees collected are of a *variety* of ages, in order to separate age effects from environmental effects which vary over time.

4.2.2 Climate

A major alternative explanation of the observed reduction in growth is long term shifts in climate. Weather variables are available from the nearest weather station and will be used to adjust trends in growth due to any changes in weather patterns. Because of the multitude of potential climatic variables, variable selection techniques will be used in a preliminary analysis to select the most important.

4.2.3 Site specific factors

Permanent stand effects will be removed by including plot in the model as a random effect. This will account for permanent stand effects due to site specific characteristics such as soil, grade, and permanent climate effects.

4.2.4 Year and Region

If the above known factors do not account for all the low frequency variability, especially if there is a decreasing trend with time, there is evidence that there may be some factor as of yet unaccounted for. However, since the regions differ in many other aspects such as climate, physiography, geology and soils, it is likely that ecotypic and/or clinal ecotypic variation with respect to growth rate exists across the range of sugar maple in Ontario.

4.2.5 Year by Region interaction

The observed differences (if any) across the pollution gradient can be investigated by testing the year by region interaction. If this is significant, then there is a difference in the yearly trend between the three regions which could possibly be related to atmospheric deposition.

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A4

A Method to Establish Background Concentrations of Contaminants and Nutrients in Soil and Vegetation

R.D. Jones, S. Bisessar, B. Chai, R.N. Emerson, W.I. Gizyn, M.Marsh, W.D. McIlveen,
D.L. McLaughlin, J. Nagusanti, R.G. Pearson and D. Racette
(Ontario Ministry of the Environment)

Background

The Phytotoxicology Section of the Air Resources Branch, Ontario Ministry of the Environment (MOE), in concert with the associates from the Northeast and Northwest Regions, recognized in 1971 a need to establish contaminant concentration guidelines for interpretation of environmental data. Utilizing the results of chemical analyses and available toxicological information, guidelines which were termed "Concentrations Considered Excessive" were developed for a number of contaminants in soil and plant foliage. These guidelines were utilized in Phytotoxicology investigations, with periodic revisions as deemed appropriate, notably in 1978 and 1982.

By early 1983, it had become apparent that the processes by which the Phytotoxicology guidelines had been established to date were less than satisfactory, because they varied among contaminants, were too subjective, and could not be supported by any consistent procedure or mathematical model.

After discussion among Phytotoxicology and Regional staff, it was agreed that new guidelines should be developed which would have a consistent mathematical basis and which would serve as levels which, if exceeded, would prompt further investigation on a case-by-case basis to determine the significance, if any, of the above-normal concentration(s). To this end, efforts were directed toward assembling a data base of analytical results for environmental samples collected from "background: (i.e. non-point source-contaminated) areas of Ontario".

Concurrent with these developments, a large-scale review of Ontario Regulation 308 (Air Pollution - General Regulation) was initiated by the Ministry of the Environment(1). One of the tasks of the review was the following: "Determine if Phytotoxicology standards, criteria or guidelines should be established for soil (and vegetation) deposition. Should they be incorporated in Reg. 308, or developed into a guideline?". A committee with Air Resources Branch and Regional representatives was established to examine this issue. The committee proceeded along the lines previously initiated, and developed "Upper Limit of Normal" (ULN) contaminant guidelines for terrestrial samples collected in Ontario. The concept and philosophy of the proposed Phytotoxicology ULN guidelines were then discussed at a Reg. 308 Workshop held in Toronto in November, 1985(2). The decision was made that the ULN guidelines, being statistically derived and subject to modification as new data are generated, not be incorporated in Reg. 308 but be published as a reference document(3).

As well as being a reference document in Reg. 308, the ULN guidelines, for soil, have also been incorporated in the Guidelines For The Decommissioning and Cleanup of Sites in Ontario(4) and in the proposed Dredge Material Guidelines, and the Backfill and Construction Application Guidelines.

The increased use of the ULN guidelines in other Ministry of the Environment guidelines and by other agencies and organizations and the lack of a formal review and maintenance process was brought forward by the Ontario Ministry of the Environment Materials Policy Committee(5). Accordingly, a committee, with representatives from the Phytotoxicology Section and the Northeast and Northwest Regions, was established in the spring of 1990 to completely re-evaluate the ULN guidelines.

The committee found that while the ULN guidelines were significantly better than the previous "Concentrations Considered Excessive" there still were problems with the ULN guidelines. These problems were related to the purpose for which the guidelines had originally been developed. There were problems with the land use categories, the sample categories and the model used in developing the ULN guidelines. Rather than trying to correct the problems, the committee recommended that the ULN guidelines be replaced with a new set of guidelines.

As the new guidelines were to be significantly different from the ULN guidelines a new name, "Typical Ontario Range" or "TOR", was chosen. The word "typical" does not imply acceptable the way "normal" did in the old name. "Ontario" is included in the name to indicate that the data used are only from the Ontario region. The use of "range", instead of upper limit, better reflects the new model on which the TOR's are based and how the guidelines are to be interpreted.

The TOR's are based on more and better-defined land use categories, more-specific receptor types and a model that can handle the non parametric data in the database. The new guidelines will be phased in over a two to three year period, starting in 1991, as the data become available.

Typical Ontario Range Model

There are problems with the model originally used to define the Upper Limit of Normal. The use of the mean plus three standard deviations (99.9% of the population) is not valid when the sample population is not normally distributed. As many of the data sets used were not normally distributed, the ULN guidelines determined by this method did not really represent 99.9% of the population. The second problem is the size of sample set used. Work has shown that for soils in Ontario, the number of samples needed to be within 10% of the mean 90% of the time ranges between 100 and 200 samples. Analysis of the data originally used to develop the ULN guidelines showed that using the same 10%/90% limits, the average number of samples needed would be 247. The use of 30 samples (previous minimum) could result in very poor estimates of both the mean and standard deviation for many of the ULN values.

Because of the non normally distributed nature of many of the parameters for which TOR's are to be developed and the lack of adequate statistics to handle non normal distributions properly, the use of parametric statistics in the new TOR model will be limited. The model for the new TOR will be based on the actual distribution of the data for each parameter/receptor/land use combination. The actual distribution was chosen over the range or minimum and maximum as the distribution will give the investigator more information on which to interpret results.

The data used to develop each TOR guideline will have to represent each of the MOE Regions. A minimum of 10 data points in each distribution will come from each MOE Region. In some cases, a receptor may not occur in a region, in which case, this will be noted and the TOR guideline will not apply to that Region.

In order to ensure sufficient sample size there must be enough data to be able to estimate the mean with a confidence interval of 10% and a confidence level of 90% or 50 data points, which ever is larger. The sample size is estimated using the Stein's Two-Stage Sample using the above confidence level and confidence interval. This will be the only parametric statistical test that is used in the TOR model (see (10) for a detailed description of the test). While this test is not necessarily valid for non parametric data, it is the best means of determining if there is sufficient sample to develop a TOR guideline.

Each datum point in a TOR distribution will represent a sample station. There will have to be a minimum of two samples collected from a station for that station to be included in a TOR distribution. The average of all the sample results from a station will be used. When calculating the average value for each sampling station, a result reported as <T will be used as is and a result reported as <W or < will be halved (see (8) for definition of <W and <T). A station must be in the Station Definition File (SDF) on the MOE SIS database to be included in a TOR distribution. In addition, each station must be a Control Sample Station (not influenced by a point source) for that land use category, as defined by the Phytotoxicology QA/QC Criteria Document (9).

As much of the TOR data will come from the re-analysis of archived samples, limits have to be placed on the number of samples used in order to minimize test loads. If a site was sampled in more than two years and replicate samples were collected in each year, then only one sample from each year, for a maximum of five years, will be used. If there is only one to two years of samples then duplicates for each year will be used. Where there is insufficient sample in one replicate, the replicate samples for that collection date may be combined. For archived samples, a site is defined as all samples collected within a 100 m radius.

It is the policy that as few as possible TOR's be developed by combining receptor/land use data sets in a statistically defensible manner. When it is determined that there is no significant difference between the distributions for two or more receptor types and/or land use categories for a given test parameter, the distributions will be combined into one and be identified as such. If it is determined that there are significant differences between the distributions for a receptor type for a given test parameter due to Regional differences, then a separate TOR guideline will be developed for each Region.

A set of data for a receptor/landuse category does not have to pass the 10/90 criteria of the Stein's Two-Stage Sample test in order to be tested against another set of data to determine if the distributions are different or similar. If they are similar they can be combined into one class.

The differences or similarities between distributions will be determined by using the Kolmogorov-Smirnov Two-Sample Test (see (10) for a detailed discription of the test). This is a non parametric statistical test that determines whether two distributions have the same mean, standard deviation and shape.

In addition to the TOR distribution, a value referred to as the TOR_{98} will exist for each parameter/receptor/land use combination. The TOR_{98} will be a value that represents the lower 97.5 percent of the sample population. The 97.5 percent was chosen as it is equivalent to the mean plus two standard deviations of a normally distributed population. The equivalent of two standard deviations was used instead of the three standard deviations used in the ULN guidelines as it was felt that it was not possible to guarantee that all of the data in a distribution are true controls. By excluding the upper 2.5 percent of the distribution, most potential outliers should be excluded. The TOR_{98} value will be similar to the ULN value and can be used in a similar manner.

For interpretation purposes, all TOR's for each parameter/receptor/land use combination will be represented graphically. Each distribution will consist of a bar showing the percentile distribution, TOR_{98}, mean, detection limit range and a phytotoxicological threshold level (if referenced ones exist). All the land use categories for each parameter/receptor will be included in one graph. For a more detailed description of the graphical representation, see Figure 1.

Land Use Categories/Receptors/Parameters

The sections below describe ten land use categories, 18 possible receptor types and 32 test parameters that will be used in developing TOR's. The potential number of TOR's that can be developed when combined using theses categories is 5760. With ten land use categories on each graph, this will mean there will potentially be 608 pages of graphs for the fully developed TOR's. While the combining of landuse categories and receptor types when no significant differences exist will reduce the total number, the amount of work involved is considerable when compared to the ULN guidelines. Between 250,000 and 500,000 test results will be required from historical data, archived samples and newly collected samples.

Land Use Categories

The two land use categories of Rural and Urban as defined in the ULN guidelines are too broad. Land use categories that represent the different degrees of contamination due to normal human activity, past and present, are needed. The following land use categories will be assessed for TOR development:

1. URBAN	A. Old Urban	A1. Residential
	(>40 years)	A2. Parkland/Greenbelt
		A3. Commercial/Industrial/Transportation
	B. New Urban	B1. Residential
	(<40 years)	B2. Parkland/Greenbelt
		B3. Commercial/Industrial/Transportation
2. RURAL	1. Residential	
	2. Parkland/Greenbelt/Woodlands	
	3. Commercial/Industrial/Transportation	
	4. Agricultural	

The definition of Urban for the TOR's is not based on an arbitrary population size as it is in the ULN guidelines. Instead Urban is defined on size and density relationship. Urban is defined as any community that is fully serviced by both municipal water and sewage systems. The requirement for water and sewer services in any community is largely determined by the size of the population and the density of the housing. It is relatively easy for an investigator to determine if the services are available. Defining Urban as areas being fully serviced by municipal water and sewage services is a common practice in the Ministry of the Environment.

Urban was split into Old Urban and New Urban because many communities, such as Mississauga, Brampton and Pickering, have been built in the last 40 years, post World War II. They have not had time to accumulate the same amounts of contaminants from normal anthropogenic activities as have the old urban areas. All areas not classed as Urban are considered Rural.

Residential property includes a dwelling and associated gardens and lawns up to the dwelling side of the sidewalk or to 3 m from the road where a sidewalk does not exist.

Commercial/Industrial/Transportation includes all properties used for industrial or commercial businesses, and all designated transportation right-of-ways. For residential roadways, this would include the 3 m road allowances. Highways would include all land between the Ministry of Transportation fence lines. For railways, it would include the land between the railway fence lines or where fences are not used the area kept clear by the railway (sprayed/mowed).

Agricultural includes all land actively used as tilled cropland or pasture. Active is defined as land tilled within the last 25 years. Land not tilled within 25 years is considered Parkland. Field fence lines, although not tilled, are to be considered agricultural. Agricultural soil guidelines are to be for 0-15 cm, cultivated, depth (See Section on Soil Below).

Parkland is everything that is not residential, commercial/industrial, transportation rights-of-way, or active agricultural land. This would include parks, utility rights-of-way, golf courses, cemeteries, schools, forests or woodlots and most large undeveloped areas.

The designations for Residential, Commercial/Industrial/Transportation, and Parkland/Greenbelt are the same for all three (Old Urban, New Urban and Rural) major land use categories. Agricultural only applies to Rural. Thus, if an area is inside a municipal border but is agricultural, it is considered Rural.

Where there is no significant difference between the distribution of data for two or more land use categories for a given receptor/parameter, the categories will be combined into one.

No TOR sampling is to be conducted in areas which can not be classified. Consequently the TOR's can not be applied to samples from unclassified land use areas.

Receptor Types

Unless otherwise stated, TOR's will be developed for the major receptor groups listed below. These are essentially the same as in the ULN guidelines except that in the TOR's the groups are further broken down into sub groups, especially in the case of vegetation. This was deemed necessary as not all receptors accumulate contaminants at the same rate and they can also have different baseline levels. Where no significant differences are found between groups, the data will be combined into one TOR covering both groups.

Due to the large number of sample types and land use categories for which TOR's are to be developed, they will be created on a priority basis. The order of priority will be determined by examining the historical data to determine what sample types were collected most frequently and what land use categories were sampled most.

As the TOR's are more specific than the ULN guidelines, the TOR's can not be applied to receptors other than those for which TOR's are developed. Where TOR's do not exist for a receptor, then the old ULN guidelines may be applied. However, good control samples would be more appropriate.

Vegetation

Combining different species into one ULN and then applying that ULN to all species is not acceptable because there are distinct differences between species or families in the amount of chemical accumulation/retention that occurs. TOR's for the following most commonly collected sample types will be developed initially:

Deciduous[a] Foliage	1) maple[1] 2) birch[2] 3) aspen/poplar[3] 4) ash[4] 5) alder[5] (NE & NW only) 6) hazel[6] (NE & NW only)
Coniferous[b] Foliage	1) spruce[7] 2) pine[8] 3) cedar[9]
Grass[c]	1) green 2) mixed 3) dry
Lichens and Moss[d]	
Garden Vegetables	

[a] -Deciduous foliage includes the blade plus the petiole. All foliage in a shoot, all ages, are to be used in the sample.

[1] -maple include: Manitoba, mountain, Norway, sugar, silver, and red maples.

[2] -birch include: white and yellow birch.

[3] -aspen/poplar include: all *Populus* sp.

[4] -ash include: black, green, white and red ash.

[5] -alder include:speckled alder

[6] -hazel include:beaked hazel

[b] -The TOR guideline for coniferous foliage is to be develop for current year needles, with the exception of cedar (all non woody tissue), with the potential for expansion to older needles at a later time.

[7] -spruce include: all *Picea* sp.

[8] -pine include: all *Pinus* sp.

[9] -cedar include: white cedar

[c] -Green grass is classed as 90% or more of the sample being green. Dry grass is classed as 90% or more of the sample being dry. Mixed is all other combinations of green and dry grass. Only grasses are to be included, no sedges or rushes.

[d] -While there is a need for TOR values for lichens and mosses in the Northern Regions, further investigation as to which species should be included will have to be conducted.

Where there is no difference in the data distribution for two or more sample types for a given test parameter/land use category these will be combined into one TOR. Conversely, if there is a significant difference between one of the species in a sample category and the rest of the species in that category for a given test parameter/land use, a separate TOR will be developed for that species/parameter/land use.

The TOR's will only use data from unwashed samples and thus can only be applied to unwashed samples. For washed samples, control samples should be taken for comparitive purposes.

Tentatively, the TOR's for deciduous and coniferous foliage and grass can only be applied to foliage collected between June 15 and September 15 for the Southern Regions and June 30 and September 1 for the Northern Regions. A study will be conducted to determine what, if any, changes occur in all test parameters over the growing season in a number of deciduous and coniferous tree species. Other seasonal limits may be placed on specific species and/or test parameters if required.

A review of the 1987 SIS records showed that garden vegetables are the fifth most commonly collected receptor type for chemical analysis by the Phytotoxicology Section. TOR's will be developed for garden vegetables after a thorough analysis of the SIS records from 1981 to 1990 to determine which of the many garden vegetables require TOR's. TOR's for garden vegetables will be limited to the three residential land use categories and possibly the Urban Parkland category.

Soil

TOR's for soil will only apply to the 0-5 cm depth, except for tilled areas (gardens and fields), 0-15 cm depth. Guidelines for the following three soil classes will be developed.

Soils Class 1) Organic carbon content <17%, sand >70% and clay >15% by weight
(all soils not in class 2 or class 3)
2) Organic carbon content >17% by weight
3) Sand content >70% and clay <15% by weight
(sandy loam and sand soils as defined in (11))

Clay and sand content is determined in the field by each investigator using the standard "Finger Assessment of Soil Texture" method (11). Organic content as determined by loss on ignition.

Due to the different ability of these soil classes to retain contaminants, there is a potential for significant differences between these three soil types. Further study will determine the actual significance. Initially, all existing soil data and archived samples, 0-5 cm, will be used and considered as being in Soil Class 1.

Snow

TOR's for snow samples will be developed for the Northeast and Northwest Regions only. These will be for snow samples collected using the standard Phytotoxicology technique (6) in which the entire snow profile is collected. The TOR will be expressed on an area loading basis (mg/m2/day) and not on the weight per volume basis (mg/l) used in the ULN guidelines.

Moss Bags

There are potential problems with developing TOR's for moss bags. The major problem is that the background level of a number of elements can vary significantly with the source of the moss. Thus, each new batch of moss may have a different starting level. As the exposed control moss bag accumulation is small, significant differences between batches can greatly affect the TOR guideline. There also may be problems in the interpretation of any data from moss bags that come from batches not included in the TOR. The other problem is that, for some elements, the level in exposed control bags is often lower than unexposed bags.

Because of the above problems, plus the fact that moss bags are really an artifical tool and not a naturally occuring receptor it has been decided that TOR's will not be developed for moss bags. As it states in this document that ULNs will be used were TOR's do not exist, and as there are ULNs for moss bags, the ULNs for moss bags will be rescinded as of the publication of the Version 1.0 of the TOR document.

Analytical Parameters

The analytical parameters for which TOR's will be developed (vegetation, soil, moss bags and snow) are given in Table 1. TOR's may be developed for tritium and radium for certain sample types if the data become available from a Federal/Provincal cooperative study.

TOR's will not be developed for organic compounds at this time. The reliability of the old data is questionable. The number of samples per receptor needed is unknown. The number of potential compounds is large. The cost, especially for PAHs and dioxins, of developing TOR's for organics would be large. A demonstrated need for a TOR guideline will be required on a compound by compound basis before the necessary work and resources will be committed to developing a TOR guideline for any organic compounds.

For reference purposes, the instrumentation, sample digestion and/or preparation and the minimum sample weight currently used by the Laboratory Services Branch, Inorganic Trace Contaminants Section, for each test will also be given. All samples collected for TOR's should have four times the minimum weight required for analysis. This will allow enough sample for re-analysis by the lab and for archiving of the sample for future analysis.

The inorganic analytical parameters for which TOR's will initially be developed, for the three major receptor types Vegetation, Soil and Snow, are listed in Table 1 below.

Table 1: Analytical Parameters for Which TOR's Will be Developed for Vegetation, Soil and Snow

Test Parameter	Vegetation Foliage & Grass	Soils 0-5 cm	Snow
Aluminum	X	X	X
Antimony	X	X	X
Arsenic	X	X	X
Barium	X	X	X
Beryllium	X	X	X
Boron	X	X	
Cadmium	X	X	X
Calcium	X	X	X
Chloride	X	X	X
Chromium	X	X	X
Cobalt	X	X	X
Copper	X	X	X
Fluoride	X	X	X
Iron	X	X	X
Lead	X	X	X
Magnesium	X	X	X
Manganese	X	X	X
Mercury	X	X	X
Molybdenum	X	X	X
Nickel	X	X	X
Total Nitrogen	X	X	X[a]
Total Phosphorus	X	X	X
Total Potassium	X	X	X
Selenium	X	X	X
Silver	X	X	
Sodium	X	X	X
Strontium	X	X	
Sulphur	X	X	X[b]
Titanium	X	X	X
Uranium	X	X	X
Vanadium	X	X	X
Zinc	X	X	X
Conductivity			X
Sus. Solids			X
Dis. Solids			X
Tot. Solids			X
Dis. Org. Carbon			X
Dis. Inorg. Carbon			X
Part. Tot. Carbon			X

a - nitrogen as nitrate, b - sulphur as sulphate

Review and Maintenance Process

Because of the scope of the TOR's, it will take a number of years to develop TOR's for all of the receptor type/land use combinations. In addition, new sample types and parameters will be added as the need arises. The TOR's will be a continually evolving set of guidelines. This will require the TOR committee be a regularly sitting body that will provide the basis for regular review and maintenance of the TOR's.

The committee will consist of one representative from the NE and NW Regions and six representatives from the Phytotoxicology Section. A minimum of half of the members should be regular field investigators to ensure that their requirements are being met.

The TOR committee will hold a series of meetings starting in the beginning of each calendar year to evaluate the data collected in the previous year for inclusion into the TOR's. The committee will also develop a work plan for the gathering of additional data for the next field season. The committee will coordinate its efforts with the Ontario Ministry of the Environment Materials Policy Committee and other relevant committees.

In order to handle the regular updating of the TOR's, the Phytotoxicology Integrated Information Management System (PIIMS) will be modified. PIIMS will identify all new data that fit the TOR criteria and will automatically update the TOR tables and graphs at the end of each year. The TOR committee will be responsible for validating these changes.

Interpretation and Application of the Typical Ontario Range

The Ministry of the Environment "Typical Ontario Range" (TOR's) for soil, vegetation, moss bags and snow were developed by the Phytotoxicology Section of the Air Resources Branch, in concert with associates from the Northeast and Northwest Regions, to assist in the interpretation of Phytotoxicology data. The TOR's are to assist in determining whether the level of a measured parameter in a given receptor is significantly above that which would be anticipated for the level of anthropogenic activity in the area sampled (land use category). An exceedance of the TOR would indicate a potential point source of contamination.

As the TOR's are also a set of distributions, they can also be used to determine where, in the anticipated distribution, a result falls. This can be used to indicate a potential level for concern even when a result falls within the range.

These guidelines apply only to samples collected using standard Phytotoxicology sampling techniques(6), prepared using standard Phytotoxicology laboratory sample preparation techniques(7) and analysed using standard MOE analytical techniques (8). As the TOR's are developed from data collected in Ontario, or specific regions of Ontario, they only apply to terrestrial samples collected in Ontario or a specific region of Ontario.

The TOR's should not be the sole means by which results are interpreted. In interpreting results importance should be placed on the control samples that are collected and on the pattern of contamination observed in the samples. The TOR's are to assist where there is some question concerning the local background samples and/or enough samples have not been collected to determine any pattern of contamination (i.e. complaint investigations). The TOR's for each receptor/land use category assume a given range of contamination resulting from normal anthropogenic activity for that land use category. As a result, the TOR's should not necessarily be considered as acceptable levels nor do they imply phytotoxicity. The one potential exception to this rule is for the Rural Parkland/Forest land use category where it can be assumed that there has been minimal impact, except for long range transport, from anthropogenic sources.

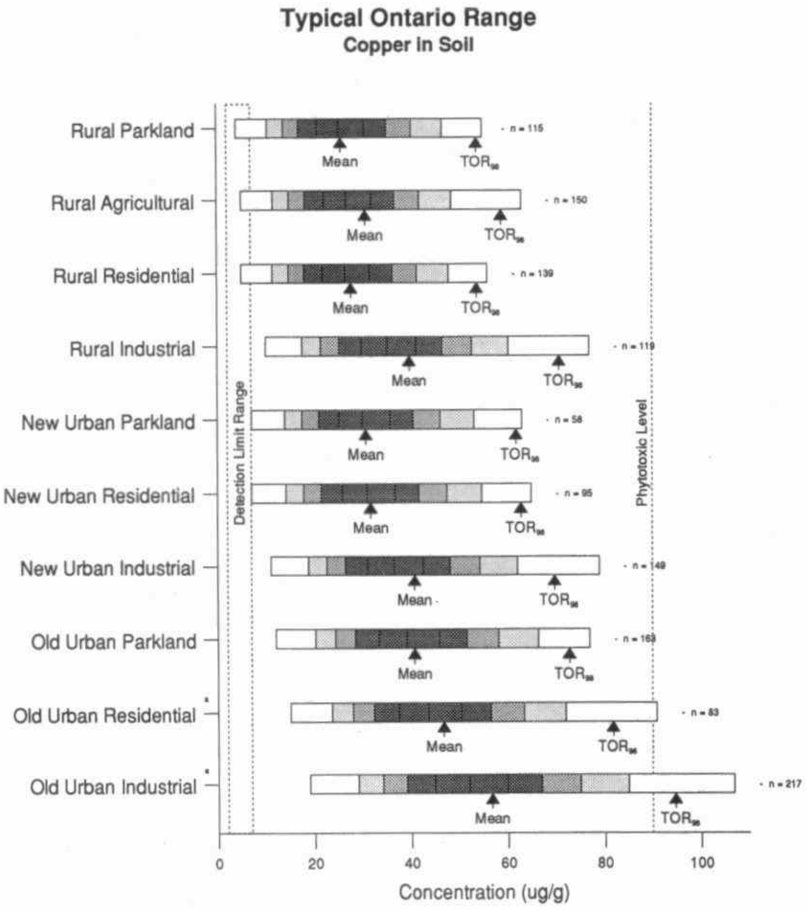
Where a TOR exists for a given receptor/land use category, the TOR will supersede the ULN for the interpretation of results. If a TOR does not exist, the ULN will be used.

The use of the TOR for purposes (i.e. incorporation into other Ministry guidelines or standards) other than those described above should be done with caution and with prior consultation with the Phytotoxicology Section.

Typical Ontario Range Distributions

No TOR's exist at this time. An example of what a typical TOR graphic will look like is given in Figure 1 below. It is anticipated that TOR's for soil and maple vegetation for the Rural Parkland land use catagory will be developed by the spring of 1991. As TOR's are developed, they will supersede the ULN guidelines for the interpretation of data. In all other cases, the ULN guidelines will be used for the interpretation of data.

Figure 1: Hypothetical Example of a TOR for Copper in Soil



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A5

FURTHER DEVELOPMENTS IN THE ANALYSIS OF THREE DIMENSIONAL ENVIRONMENTAL DATA

Philip K. Hopke and Yousheng Zeng[1]
Department of Chemistry
Clarkson University
Potsdam, N.Y. 13699-5810.

Air quality data is commonly analyzed by a variety of methods that treat the data characterizing the atmosphere at a site over time, or for a single chemical constituent over space, or over time. All of these two dimensional analyses fail to provide the full information content of the data to the investigator since the atmosphere is really represented by three dimensional data; compositional data taken at multiple sites (space) and times. To analyze such data, three dimensional statistical methods are needed. We have previously reported on our development of three-mode factor analysis. In order to provide more quantitative interpretation of data sets, we have explored the development of target transformation three-mode factor analysis. In simulated data sets representing the composition of airborne particulate matter, we have attempted to recover the original source profiles and source contributions to the aerosol mass. However, we have found that we could not adequately reproduce the data even in the absence of error. If error-free data cannot be adequately reproduced, this model cannot be applied to real world data. Thus, an alternative approach, direct trilinear decomposition, has been explored. This method also decomposes the three dimensional data matrix in a series of matrices that can be interpreted in terms of source compositions and contributions. With simulated data with and without data, excellent reproduction of the correct results were obtained. The mathematical basis of these methods along with the results of these exploratory studies will be presented.

Introduction

Dispersion modeling and receptor modeling are two types of techniques used in air quality management. Dispersion models have been used in this field for a long time. For dispersion modeling, a major effort is usually needed including a survey of emissions over the studied area, collection of meteorological data, field tests to determine the dispersion parameters, mechanistic studies on the chemical transformation and scavenging between phases, as well as the studies of the models themselves. There are a number of difficulties associated with these steps in dispersion modeling (Budiansky, 1980; Gorden, 1980, 1988). Budiansky (1980) has discussed the problems of dispersion models, for example, the error in emission inventories, the uncertainty in the horizontal and vertical dispersion parameters, low availability of complete information and high cost for complex models, etc. In addition, dispersion models can only handle the sources that are known to contribute to the system. It can not include the sources that are unknown or where lack of emission data makes a source unmodelable.

In last two decades, receptor modeling has played a larger and larger role in air quality management. Receptor models in contrast to dispersion models utilize the data collected at receptor sites to elucidate information on properties and influence of emission sources. In typical receptor models, ambient samples are analyzed yielding their chemical compositions. These data can then be analyzed so that the sources can be identified and their contributions to the collected sample mass can be estimated. This procedure is also called source apportionment. The estimates of the source contributions for an airshed are useful information in developing air pollution control strategies.

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[1] Present Address: National Environmental Technologies, Inc., 9101 Southern Pine Blvd, Suite 280, Charlotte, NC 28217

A variety of receptor models have been developed. There have been several major review articles (Gorden, 1980, 1988; Cooper and Watson, 1980), a number of symposium books (Macias and Hopke, 1981; Dattner and Hopke, 1983; Pace, 1986; Watson, 1989), and one comprehensive book (Hopke, 1985) reviewing and describing the principles and applications of these models. The ultimate purpose of receptor modeling is to qualitatively identify the pollution sources at the receptor sites and quantitatively estimate their mass contributions. A three-way table of air quality monitoring data provides information on the spatial and temporal variations of the pollutants. A model based on such a data set potentially has more power to identify the sources and estimate the contributions than the traditional methods do.

Three-Way Data Analysis

Air pollution systems are typically characterized by taking samples over time at a number of sampling sites. These samples are then characterized by a variety of analytical methods so that the data set can be represented by a data block as illustrated in Figure 1. The term "three-way data table", or "three-way matrix", or "three-mode matrix" are used to describe this kind of data

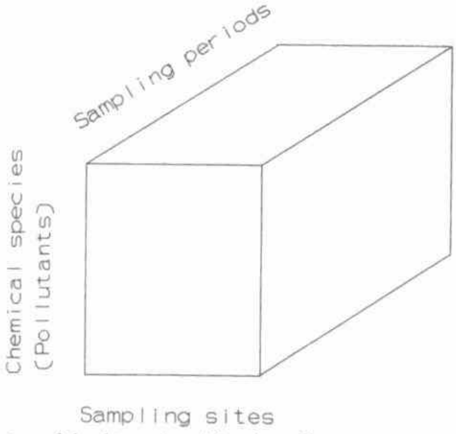

Figure 1 Typical structure of the data gathered for air quality management.

sets. Such a data set provides information on the simultaneous temporal and spatial variations in the system. However, conventional (two-mode) principal components analysis methods are really designed to analyze a data rectangle obtained by taking a slice of the block in one of the three orthogonal directions. For factor and principal components analysis, this slice is typically the measured concentrations at a single location over time. The empirical orthogonal function (EOF) approach analyzes a single species concentration over sites and time (Peterson, 1970). One can also perform a spatial analysis of elemental concentrations over sites for a single time interval. However, each of these methods is only looking at a single plane in the data block.

Another factor analysis method called three-mode factor analysis (TMFA) has been developed by Tucker (1966) and Kroonenberg (1983). This method works directly on the full three-way data matrix as its input, and thus can examine variations among all three modes simultaneously. The ability to examine three-way observational data suggests the potential utility of TMFA in receptor modeling. TMFA (Zeng and Hopke, 1990) provides a technique to analyze such a complicated system and condense the system variations in a smaller core matrix as a summary of the system. Unfortunately, TMFA could not provide the mass contributions. A modified version of Target Transformation Factor Analysis, TTFA, (Hopke, 1988) was explored by Zeng (1990). However, this approach could only achieve a semi-quantitative analysis because it does not take full advantage of three-dimensional variations. A new model called direct trilinear decomposition (DTD) can potentially overcome the problems identified with the other three-mode approaches as well as the two-mode models.

The development of a DTD model in receptor modeling has evolved from the work by Sanchez and Kowalski (1990). They developed the DTD method to process the data obtained in analytical chemistry with instruments that generate two-dimensional arrays of data for multiple samples. Their example was a three-way data set of emission-excitation fluorescence spectra for three mixtures of three organic compounds. With their DTD method, the emission and excitation spectra of all three compounds were predicted and the relative concentration of the compounds in the mixtures were calculated.

The DTD method appears to be a quantitative method for three-way data. In order to apply DTD in receptor modeling, a major difficulty had to be overcome. This problem was how to relate pollution sources to the model. In the example of Sanchez and Kowalski (1990), each organic compound had two spectra, an emission spectrum and an excitation spectrum. In fact, DTD model is applicable for a multiple sample system with two-dimensional spectral surfaces. A source profile in a receptor modeling problem can be considered to be one spectrum. Then another spectrum-like property of the pollution source is needed. This problem and others concerning the application of DTD in receptor modeling were resolved by methodological studies using simulated data sets. The results of these studies are presented in this report.

Theory of Direct Trilinear Decomposition

The trilinear model will be introduced by comparing linear and bilinear models in mathematical sense. The comparison of DTD will also be made with the general mass balance receptor models. The atmospheric mass balance problem can be expressed as a linear model.

$$x_{ijk} = \sum_{n=1}^{N} y_{in}\, z_{njk} + \epsilon_{ijk} \tag{1}$$

where x_{ijk} is ambient concentration of species i at sampling site j in period k, [ng/m^3], y_{in} is the concentration of i in the particles coming from source n, [ng/μg], z_{njk} is the mass contribution of source n at site j in period k, [μg/m^3], N is number of source types and ϵ_{ijk} is the error. This expression describes the typical multivariate linear model.

If z_n is expanded to a vector, the model become a bilinear model:

$$X = YZ + E = \sum_{n=1}^{N} y_n \otimes z_n + E \tag{2}$$

where $\boldsymbol{X}$ is a $I \times J$ two-way matrix, and $\boldsymbol{Y}$ and $\mathbf{Z}$ are $I \times N$ and $N \times J$ matrices, respectively. Their n-th column vectors are $\{y_n\}$ and $\{z_n\}$. The sign $\otimes$ represents an outer product. A term $\boldsymbol{y}_n \otimes \boldsymbol{z}_n$ (called a dyad) is equivalent to the matrix product $\boldsymbol{y}_n \boldsymbol{z}_n^T$. $\boldsymbol{E}$ is the error matrix equivalent to ϵ in the linear model [equation 1]. Considering $\boldsymbol{E}$ to be the model residual term, TTFA is actually a bilinear model.

The bilinear model can be expanded to a trilinear model by adding another term in third mode. If $\boldsymbol{a}_n$, $\boldsymbol{b}_n$, and $\boldsymbol{c}_n$ are used for the vectors in three modes, the trilinear model can be expressed as:

$$X_{ijk} = \sum_{n=1}^{N} a_n \otimes b_n \otimes c_n + E_{ijk} \tag{3}$$

Note that $\boldsymbol{X}_{ijk}$ and $\boldsymbol{E}_{ijk}$ represent three-way matrices, and x_{ijk} and e_{ijk} are their corresponding elements. The number of elements in the vectors $\boldsymbol{a}_n$, $\boldsymbol{b}_n$, and $\boldsymbol{c}_n$ are I, J, and K, respectively.

In Sanchez and Kowalski (1990), $\boldsymbol{X}_{ijk}$ was a three-way data table with the i mode for emission wavelength, the j mode for excitation wavelength, and the k mode for sample. With DTD, the data set was decomposed into $\boldsymbol{a}_n$ standing for emission spectrum of compound n, $\boldsymbol{b}_n$ for excitation spectrum of compound n, and $\boldsymbol{c}_n$ for relative concentration of compound n in the samples. The compounds were identified by their spectra ($\boldsymbol{a}_n$ and $\boldsymbol{b}_n$), and their relative concentrations were obtained in $\boldsymbol{c}_n$.

The trilinear model may be considered to be a special case of TMFA model (Zeng and Hopke, 1990). Equation 3 can be rewritten in scaler form.

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + \epsilon_{ijk} \tag{4}$$

The trilinear model is also called Parallel Factor Analysis (PARAFAC) or CANDECOMP model in the psychology literature (Kroonenberg, 1983; Harshman, 1970, 1976; Carroll and Cheng, 1970). The procedure for performing a trilinear decomposition based on the model in equation 3 is given by Zeng (1990) and is based on the work of Sanchez and Kowalski (1990).

DTD Applied in Receptor Modeling

The key to applying DTD in receptor modeling is to establish the relationship between the terms in the model [equation 3] and the physical properties of the airshed. If the three-way data matrix is arranged such that mode 1 (*i*) corresponds to the chemical species, mode 2 (*j*) to sampling time, and mode 3 (*k*) to site, the *N* vectors $\{\boldsymbol{a}_n\}$ can represent the source profiles. Two new concepts are introduced so that the model can be fitted into the physical system. "Emission pattern" is used to reflect the relative variations of source emission strength changing with time at the receptors. Like a source profile, the emission pattern can be considered to be another property of a source. Each source has its own emission pattern. With the source profile and emission pattern, a source can be characterized more completely and accurately. The vectors $\{\boldsymbol{b}_n\}$ in the model then correspond to the emission pattern.

Another concept, the site coefficient, is introduced to refer to the vectors $\{\boldsymbol{c}_n\}$ in equation 3. The site coefficients indicate the variation in source strength from site to site. With these definitions, a three-way air quality data set could be decomposed into source profiles ($\boldsymbol{a}_n$), emission patterns ($\boldsymbol{b}_n$), and site coefficients ($\boldsymbol{c}_n$). The mass contribution of source *n* at site *k* in time *j*, $\bar{z}_{njk}$, can be obtained by combining the emission pattern and the site coefficient.

$$\bar{z}_{njk} = b_{jn}c_{kn} \tag{5}$$

If the source profile $\bar{y}_{in}$ is defined as

$$\bar{y}_{in} = a_{in} \tag{6}$$

the model in scaler form becomes:

$$x_{ijk} = \sum_{n=1}^{N} a_{in}b_{jn}c_{kn} = \sum_{n=1}^{N} \bar{y}_{in}\bar{z}_{njk} \tag{7}$$

The scale of $\bar{y}_{in}$ and $\bar{z}_{njk}$ do not necessarily agree with the actual scale of source profiles and contributions. Similar to TTFA, a regression procedure can be used to find a set of scaling coefficients, $s=\{s_n\}$, such that

$$x_{ijk} = \sum_{n=1}^{N} \left[\frac{\bar{y}_{in}}{s_n}\right](s_n\bar{z}_{njk}) = \sum_{n=1}^{N} y_{in}z_{njk} \tag{8}$$

where y_{in} and z_{njk} are the scaled source profiles and contributions. The regression is based on

$$mass_{jk} = \sum_{n=1}^{N} z_{njk} = \sum_{n=1}^{N} s_n \bar{z}_{njk} \tag{9}$$

Studies with Simulated Data Sets

The DTD method was tested with simulated data sets. A simulated data set was created using the same three source profiles as used in the second simulated data set presented by Zeng and Hopke (1990). Twenty species were considered. It was assumed that the emission pattern of source 1 is a random pattern, and the pattern of sources 2 and 3 are periodic with different periodicities. Figure 2 shows these patterns, along with the formulae used to generate them. Mode 2 contains 18 sampling periods. Assume there are 4 sites with site coefficients assigned in Table 1. The simulated data set was produced using equation 1. The contributions, z_{njk}, in equation 1 were obtained from the emission patterns and site coefficients.

The DTD method was applied to the simulated data set without added errors. The results were perfect. Both the source profiles and source contributions estimated by the model were exactly same as the true values. Several other simulated data sets with different source profiles were tested and the model gave the same excellent results. These tests show the general validity of proposed method.

Tests need to be made to investigate the sensitivity of the model to the possible error components existing in the system. The primary error components in the system include measurement errors in the ambient concentrations (i.e. errors in X_{ijk}), and possible fluctuations in the source profile concentrations (y_n). Collinearity is another important factor that may cause large errors in the model output. Collinearity problems occur when two or more sources have similar source profiles. The correlation coefficient between two source profiles can be used to measure their similarity.

In order to investigate the influence of these factors, two more simulated data sets were created in addition to data set I. The only difference between data sets II and III and data set I is the source profiles. Source profile 2 in these data sets was created in such a way that the

Table 1 Site coefficients for the data set IV

Site	Source 1	Source 2	Source 3
1	50	50	50
2	50	50	100
3	100	50	100
4	150	150	200

correlation coefficients between source 1 and source 2 increase from 0.525 in data set I to 0.836 in data set II, then to 0.977 in data set III. These source profiles are listed in Table 2.

Errors were added to the simulated data sets. Two types of errors were considered. One was the errors associated with ambient sampling and analysis. The other was fluctuations of the

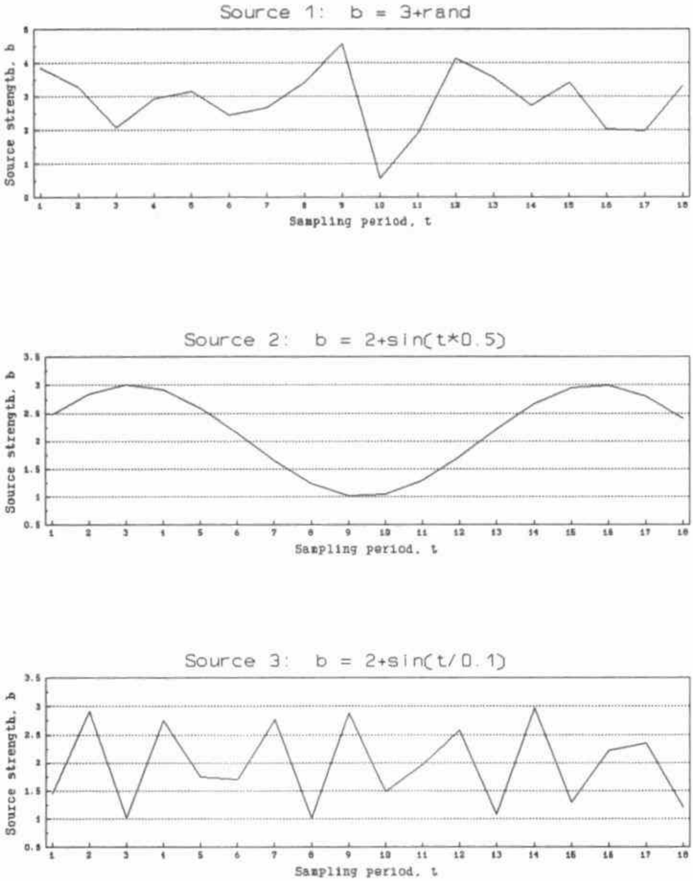

Figure 2. The source emission patterns used in the simulated data sets.

Table 2 Source profiles used in the data sets I, II, and III

No.	Element	Source 1	Source 2			Source 3:
			in set I	in set II	in set III	
1	Na	9.7	5.9	5.9	5.9	1.4
2	Al	26.	8.8	17.6	13.2	2.5
3	Si	150.	47.	105.5	61.3	5.
4	S	15.	71.	71.	18.8	40.
5	Cl	11.	12.	12.	8.8	11.
6	K	10.	6.3	6.3	6.7	5.
7	Ca	23.	11.5	11.5	14.5	5.
8	Ti	2.6	1.7	1.7	1.7	2.8
9	V	0.48	1.7	1.7	0.7	0.01
10	Cr	0.4	0.9	0.9	0.4	1.
11	Mn	0.48	6.5	6.5	0.5	0.22
12	Fe	18.	10.7	10.7	10.7	44.
13	Ni	0.2	0.7	0.7	0.7	250.
14	Cu	1.3	3.2	3.2	0.7	2.
15	Zn	3.2	32.	32.	1.9	1.9
16	As	0.3	3.	3.	0.3	0.05
17	Se	0.11	1.1	1.1	0.05	0.05
18	Br	0.2	1.3	1.3	0.05	0.84
19	Sb	0.03	0.9	0.9	0.05	0.05
20	Pb	2.	8.2	8.2	1.2	10.

source profiles. The notations e_x and e_y are used for the former and latter errors, respectively. The errors were added by the following equation:

$$x_{ijk} = \sum_{n=1}^{N} (y_{in} + e_y^{(ijk)})\, z_{njk} + e_x^{(ijk)} \tag{10}$$

The errors $e_y^{(ijk)}$ and $e_x^{(ijk)}$ were normally distributed random numbers. A random number generator was invoked for every i-j-k combination. The magnitude of the errors is controlled by a parameter h:

$$\begin{aligned} e_y^{(ijk)} &= h_y\, y_{in}(rand) \\ e_x^{(ijk)} &= h_x\, x_{ijk}(rand) \end{aligned} \tag{11}$$

where *rand* is a random number generator producing normally distributed random numbers with a mean of 0 and a standard deviation of 1, e.i. $N(0,1)$. Source profile variations are more likely to

Table 3. Descriptions of the simulated data sets used for DTD tests

Simulated data set	Highest correlation coefficient between source profiles	error level in ambient measurement, h_x (%)	error level in source profiles, h_y (%)
I	0.525	0	0
I(A)	0.525	1	0
I(B)	0.525	1	1
I(C)	0.525	4	0
II	0.836	0	0
II(A)	0.836	1	0
II(B)	0.836	1	1
II(C)	0.836	4	0
III	0.977	0	0
III(A)	0.977	1	0
III(B)	0.977	1	1
III(C)	0.977	4	0

be log-normal than normal (Currie *et al.*, 1984), but normally distributed errors were used in these preliminary tests. If h_y is chosen to be 0.01, there will be roughly 1% fluctuations around the true y_{in} values. These modifications to the data sets were designed to simulate the real situation in the atmosphere. The source profiles may fluctuate around the mean values from time to time and site to site. After the particles are collected in a sample with a certain mass and an actual chemical composition, there will be errors in measuring that composition. This simulation method was used in all three data sets with different error levels. The data sets generated from same base (same true source profiles and contributions) are designated with letter "(A)", "(B)", "(C)", ... following the notation of the base set (Table 3). For example, data set I is a base set (error-free). Data set I(A) is from the same base with 1% level of errors added in X_{ijk} matrix.

The DTD method was applied to these simulated data sets. The results are summarized in Table 4. The correlation coefficients between true and estimated source profiles indicate how close the estimated profile are to the true profiles. The APPRAE [see Zeng and Hopke, 1990] is used to measure the goodness of model estimation of source contributions. As mentioned before, the DTD method always gives the true solutions for error-free data sets. When errors exist in the data sets, the method identified the sources very well and the estimated source contributions were reasonably good. The APPRAE values increase as error is added at higher and higher levels. For same error level, the error in the model estimation increase as the collinearity increases (from data set I to III). Note that when the two sources are highly collinear (correlation coefficient of

Table 4 Results of DTD and TTFA for the simulated data sets

Simulated data set	Source profiles: the correlation coefficients						Source contributions: APPRAE (%)	
	DTD			TTFA			DTD	TTFA
	S1	S2	S3	S1	S2	S3		
I	1	1	1	1.00	0.98	1.00	0	9.56
I(A)	1.00	1.00	1.00				2.77	
I(B)	1.00	0.99	1.00	1.00	0.95	1.00	5.35	14.95
I(C)	0.98	0.89	1.00				10.89	
II	1	1	1				0	
II(A)	1.00	1.00	1.00				11.30	
II(B)	1.00	1.00	1.00	1.00	0.99	1.00	10.34	14.48
II(C)	0.94	0.97	1.00				71.41	
III	1	1	1				0	
III(A)	1.00	0.97	1.00				13.46	
III(B)	1.00	0.98	1.00				13.06	NS[a]
III(C)	0.99	0.98	1.00				58.37	

a: NS = No solution (source not identified or large negative mass estimated).

0.977), the model still can identify the sources and estimate the contributions in a reasonable range. In analyses of data sets III(A) and III(B), it is nearly impossible to identify sources 1 and 2 by looking at the estimated source profiles (y_n or a_n). However, the two sources can be distinguished by examining their emission patterns (b_n). This result shows a unique feature of DTD model.

Several data sets were also analyzed by TTFA to compare the TTFA and DTD models. The TTFA was performed individually on each slice of the data set. The analysis was in Q-mode. Since the iterative target transformation did not produce source profiles as well as DTD did, there were larger errors in estimated contributions. When two sources were highly collinear, TTFA failed. TTFA identified only two sources. If three sources were retained, the contributions of one source were large negative values. All of the comparisons in Table 4 show that DTD performed better than TTFA.

Another advantage of DTD method is that there are no trial and error procedures involved. In TTFA, the modeler needs to decide which target vector or vectors produced by the iteration from unique vectors should be selected. The results will depend on these selections. The combination of these vectors for final results is also trial and error based method. It is usually time consuming. The DTD procedure is straight forward, and it is more objective. The

DTD is more efficient because it analyze the whole three-way data set at once.

The DTD model does not require prior knowledge of the sources. An alternative approach to solving equation 1 is to use a regression analysis with known source compositions. This approach is called a Chemical Mass Balance (CMB) analysis. However, the modeler needs to know what kind of sources exist in the system, and what their source profiles are. The results rely heavily on the quality of the source profiles inputed into the model. However, it is often difficult to find suitable and accurate source profiles. In practice, collinearity is also a problem with CMB (Cheng *et al.*, 1988). DTD is potentially a useful method to overcome the collinearity problem because of the additional dimensions that can be examined.

In all receptor models, it is assumed that the chemical compositions of the sources (source profiles) are constant from sample to sample. In a real atmospheric system, the source profiles will fluctuate around their means. The bigger the fluctuations, the larger the errors will be in the model estimations. The DTD model requires the same assumption. In addition, the DTD model also requires that the source emission patterns are same for all sites. For instance, if the source strength goes down by 30% from sampling period 1 to period 2 at one site, the same percentage decrease should be observed at other sites although each site may have its own absolute value. This assumption implies that local influences on the sites should be minimized when designing the sampling network.

Conclusions

A basic methodological study of direct trilinear decomposition as a receptor model has been conducted. The DTD model results showed some very attractive features, including the capability to distinguish similar sources, better accuracy and simpler procedures compared with TTFA. More methodological studies are needed, for example, a study of the determination of the number of sources (*N*). The number of sources could be determined based on the eigenvalues or based on some type of residuals analysis. Sanchez and Kowalski (1990) suggested "that a slight overdetermination of *N* does not affect the resolved spectra as much as underestimation", but they did not give a better way to resolve this "elusive" question. Applications to real data sets will then be needed to see how effective the approach can be in resolving the full complexity of the receptor modeling problem.

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EVALUATING THE COMPREHENSIVE MODEL ADOM

C. FUNG, R. BLOXAM, P.K. MISRA AND S. WONG

ONTARIO MINISTRY OF THE ENVIRONMENT
125 RESOURCES ROAD, REXDALE, ONTARIO

1. Introduction and Brief Model Description

The Acidic Deposition and Oxidant Model (ADOM) was developed to study the response of acidic deposition to various emission scenarios. Before the model can be applied with confidence, its simulation of the current verifiable scenarios must be evaluated. This paper briefly describes three such tests. The details of ADOM development are given in ERT (1984).

ADOM is a three-dimensional Eulerian model with 12 vertical layers extending from ground up to 10 km and for a horizontal grid spacing of 127 km by 127 km over the 33 x 33 grid domain depicted in Figure 1.

The modules in ADOM are:

Transport: advection and diffusion in 3-D based on a cell-centred flux formulation.

Gas-phase Chemistry: 47 species involved in 114 species representing the major sulphur, nitrogen and oxidant reactions.

Cloud Physics: cloud transport and mixing simulated by a stratiform and a cumulus module with parameterized cloud microphysics.

Aqueous-phase Chemistry: 13 air and aqueous species involved in 25 chemical and transfer reactions.

Dry deposition: deposition velocity modelled as the inverse sum of the aerodynamic, deposition layer and surface canopy resistances.

The input to drive ADOM are:

Emissions: SO_2, SO_4^{2-}, NO_x, NH_3 and 10 categories of reactive hydrocarbons in 3-D and with appropriate temporal variations.

Meteorology: wind, temperature, relative humidity, eddy diffusivity and cloud information, for transport, cloud and chemical processes, given in 3-D. The Canadian Meteorological Centre's spectral weather prediction model is used as a dynamic interpolator between observations. A 1-D boundary layer model enhances the resolution of these data close to the ground.

Geophysical: Land use and terrain data for dry deposition and micrometeorological calculations.

2. Model Performance Evaluations

Simulations of a spring, a winter and a summer period are presented. The first few days of each simulation are used to "start up" the model and the evaluation of the model's performance was made on the remaining days. Since the first two simulation periods have limited observational data, this paper will emphasize on the evaluations with the EMEFS data.

2.1 The Spring Simulation

ADOM was run for the period from April 10 to April 29, 1981 during the OSCAR (Oxidant Scavenging and Characteristics of April Rain) field experiment. A series of frontal disturbances tracked through the northern United States and southern Canada over the 20-day period. Shower activity dominated in the western half of the domain with a mixture of drizzle, rain and showers in the east.

Observed daily average SO_4^{2-} concentrations in precipitation were available at 34 sites in the northeastern U.S. and southern Ontario for 5 days during this period. A scatter graph of modelled versus observed SO_4^{2-} concentrations in precipitation averaged over OSCAR II (April 13-14) and OSCAR IV (April 22-24) is given in Figure 2. The average model results showed little bias and more than 70 and 80% of the modelled results were within a factor of 2 of the observations. Given possible errors in the input NH_3 and NO_x emission data as well as the fact that a modelled grid average is being compared to point measurement, these results are encouraging.

2.2 The Winter Simulation

ADOM was run for the period from January 28 to February 7, 1985 with the first day used as a startup. Model predicted SO_4^{2-} concentrations in precipitation were compared with observations from the Acid Deposition System (Figure 3). The large scatter in this graph can partly be explained by the large scatter found between model grid average precipitation and that observed at the measurement sites. Figure 3 shows that results with only a single day of precipitation over the 10-day period were worse than multi-day averages (i.e. precipitation is more consistent across a grid for a multi-day average). The nitrate/sulphate ratios in precipitation were higher during this winter episode than in the spring simulation (1.6 in winter and 0.8 in spring). This compares with the observed ratios (2.4 in winter and 0.9 in spring).

For other species observed data were very limited but the model overpredicted SO_2 air concentrations and systematically underpredicted air concentrations of sulphate and nitrate.

2.3 The Summer/Fall Simulation (EMEFS)

The Eulerian Model Evaluation Field Study was conducted over eastern North America from July 15 - October 6, 1988 to gather data in three dimensions to evaluate comprehensive models of long-range transport (Barchet and Dennis, 1989). A 12-day period from July 28 - August 8 and a 37-day period from August 25 - September 29, 1988 were simulated. Preliminary comparison of the two periods shows similar characteristics. The results of the latter period are discussed in detail below.

The monitoring sites of EMEFS are grouped into regions (see Figure 1) according to meteorological and emissions characteristics so as to provide greater clarity to the analyses. In the scatter plots presented below, the symbols refer to the regions. Each point in the scatter plot is a weighted average over the available daily observed and predicted data between August 27 - September 29, 1988.

Figure 4 presents the comparison of the modelled and observed **ground level SO_2 in air.** All but five points are overpredicted. Out of the heavy emissions area represented by Regions 2, 5 and 6, only one station shows an underprediction. The stations for light emissions area represented by Regions 1, 3, 7, 8 and 9 are mainly found in the lower half of the observed and predicted ranges.

Figure 5 presents the comparison of the modelled and observed **ground level SO_4^{2-} in air.** All except 3 points are underpredicted. The 3 points that are not underpredicted are in remote regions either upwind or downwind of heavy source areas. The values of these remote regions (1 and 3) are confined to the lower half of the predicted and observed range of values. The higher values in the plot have in general a larger absolute underprediction. The largest predicted value is 6.7 $\mu g\ m^{-3}$ while the largest observed value (not the same point) is over 10 $\mu g\ m^{-3}$. It seems like the predictions have reached a limit and cannot increase further. Analysis of the early period (July 28 - August 8, 88) shows an even more drastic trend in underpredicting at the top end.

Figure 6 presents the comparison of the modelled and observed **ground level total sulphur in air.** This is done by adding the SO_2 and SO_4^{2-} after converting them to their sulphur equivalent. This plot shows a slight overprediction. Most regions show points on both sides of the 1:1 line.

Figure 7 gives the comparison of the modelled and observed **SO_4^{2-} concentration in precipitation.** The scatter in these data is large. Nevertheless, the mean of the observed agrees with the mean of the modelled values. In other words, there is little systematic bias.

Analyses were also made on the ground level NO_2 and nitrate concentrations in air and the nitrate concentrations in precipitation. The NO_2 in air is slightly underpredicted and the nitrate in air overpredicted. These air nitrogen species show less consistent behaviour in terms of under- and overprediction than the corresponding sulphur species. These also show more scatter. The wet nitrate shows a slight underprediction with even larger scatter than the corresponding sulphur concentrations in precipitation. Since measurements of nitrogen species concentration cannot be made with very high accuracy, we will focus only on the sulphur species.

3. Interpretation of Model Performance

The EMEFS is the first time ground level air sulphur concentration has been evaluated extensively. A major explanation needed for the performance is the overprediction of SO_2 in air and underprediction of SO_4^{2-} in air.

A plot of the temporal trends of the ground level air SO_2 and SO_4^{2-} concentrations (see Figure 8 for Region 5) shows that the temporal trends of both species are captured by the model. The same level of agreement between modelled and observed data is seen for other regions. Inspection of the meteorology of Region 5 reveals that an increase in the concentration is associated with a dry period while a decrease is associated with precipitation which scavenges the pollutants. For the regions away from major sources, the wind advecting the pollutants into and out of the region also contributes to the fluctuation. Thus, the above performance suggests that the meteorology responsible for transport is reasonable. So the explanation may lie in the chemistry.

The performance of the sulphur species indicates that the total amount of sulphur in the first level is approximately correct and that SO_2 is converted to SO_4^{2-} too slowly. This can be due to two reasons:

1. A missing mechanism: Studies in Europe (e.g. Ruprecht and Sigg, 1990) have suggested that SO_2 can be converted to SO_4^{2-} in fog at a much faster rate than in dry air. Fog acts like a cloud as an aqueous-phase medium for rapid SO_2 oxidation. A preliminary study on the first 12 days of the simulation period based on weather maps shows that fog is prevalent. ADOM does not handle fog at present. However, that study also shows that fog cannot be the sole explanation.

2. Inaccurate Oxidant Chemistry: Preliminary comparison at one point in Region 2 of modelled and aircraft measured vertical oxidants (H_2O_2) profiles indicates that H_2O_2 is significantly underpredicted by the model throughout the entire column of the atmosphere. This will limit the rate at which SO_2 is converted to SO_4^{2-} both in air and in cloud.

The above suggestions are currently under investigations.

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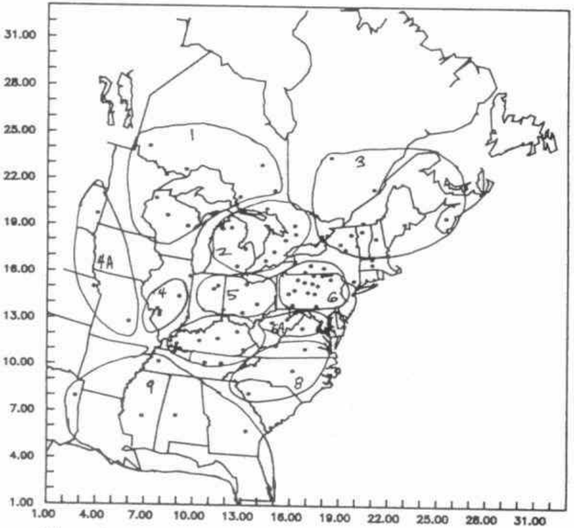

Figure 1. The ground based monitors of the EMEFS with the outline of the nine regions for our evaluations.

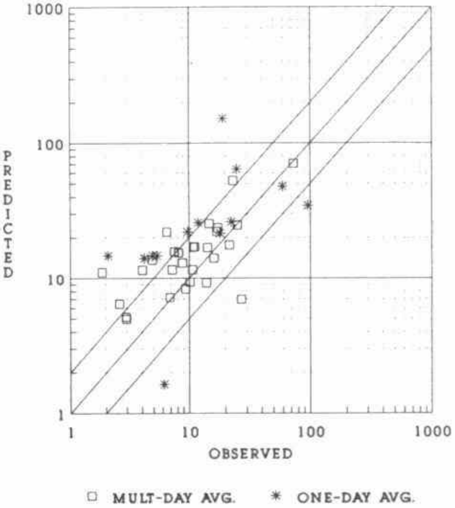

Figure 3. Comparison of event averaged observed and modelled sulphate concentration (μM) in precipitation for the winter study. The diagonal is the 1:1 line and the line on each side is the factor of 2 line.

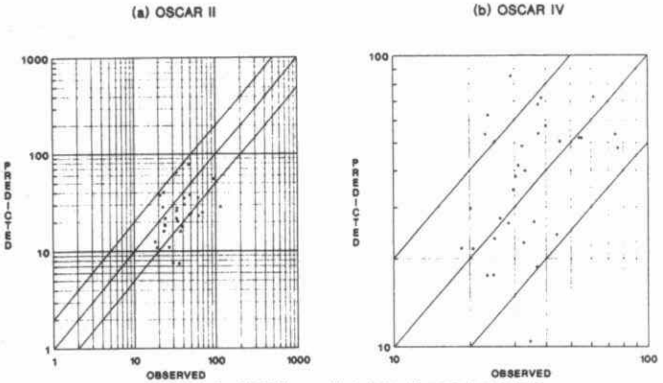

Figure 2. ADOM's predicted vs observed sulphate concentration in precipitation (uM) during OSCAR II (a) and OSCAR IV (b). The diagonal is the 1:1 line and the line on each side is the factor of 2 line.

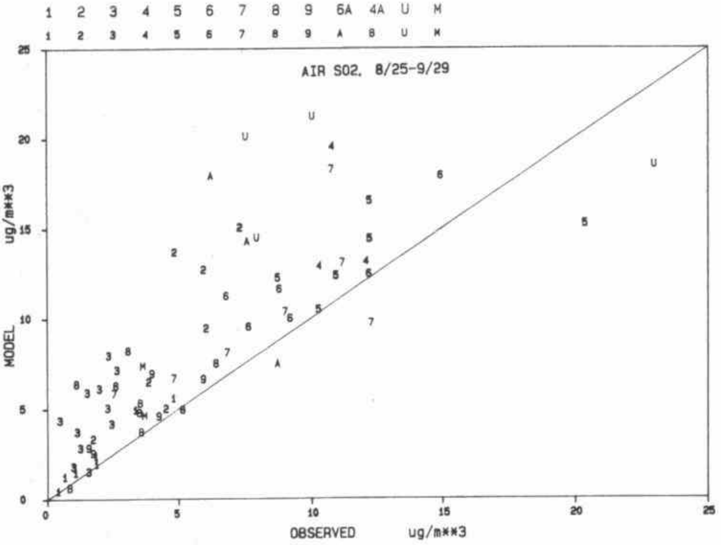

Figure 4. Modelled vs. observed ground level concentration for SO_2 for August 25 - September 29, 1988 for EMEFS.

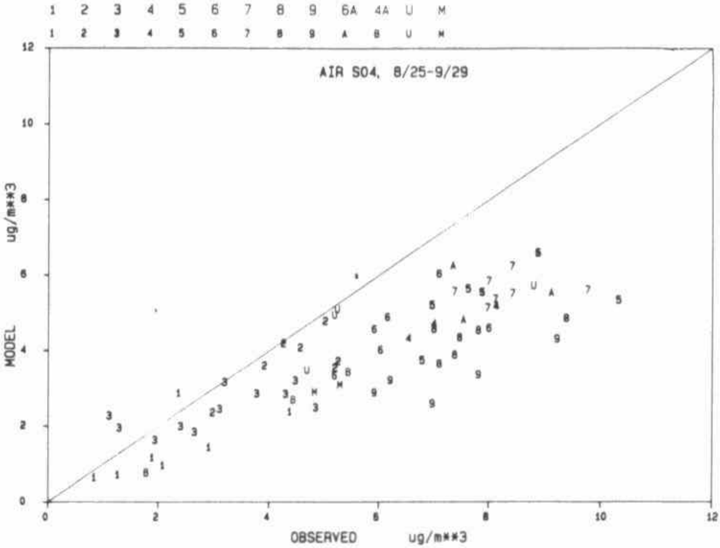

Figure 5. Modelled vs. observed ground level concentration for sulphate for August 25 - September 29, 1988 for EMEFS.

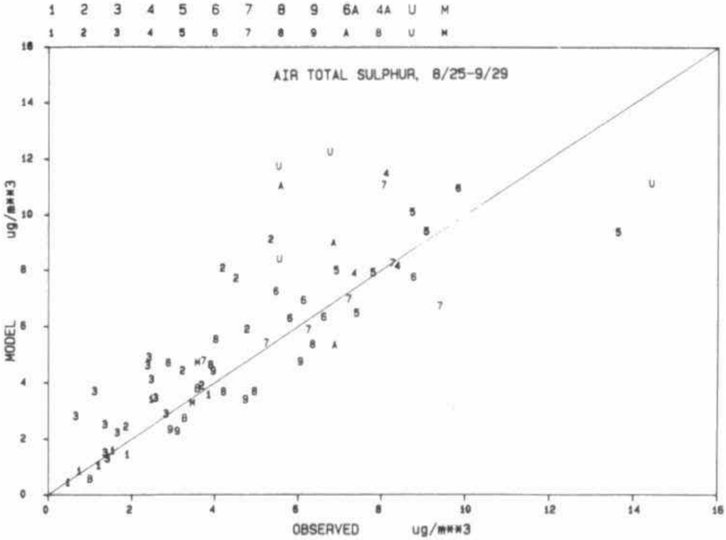

Figure 6. Modelled vs. observed ground level concentration for total sulphur for August 25 - September 29, 1988 for EMEFS.

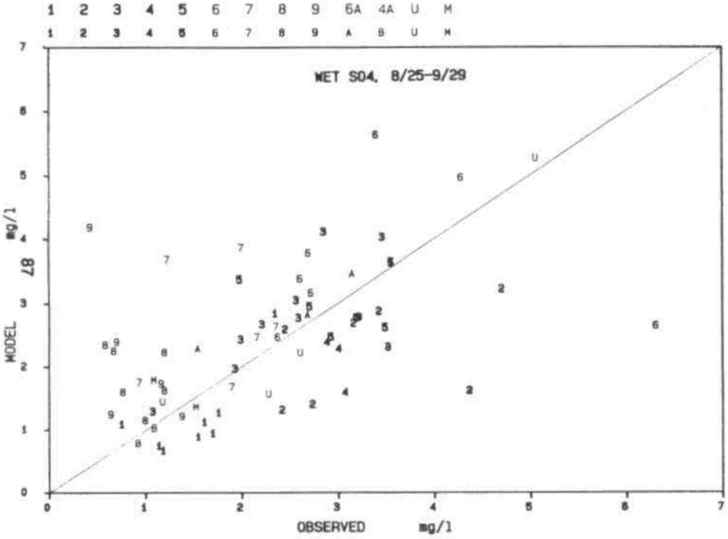

Figure 7. Modelled vs. observed concentrations in precipitation for August 25 - September 29, 1988 for EMEFS.

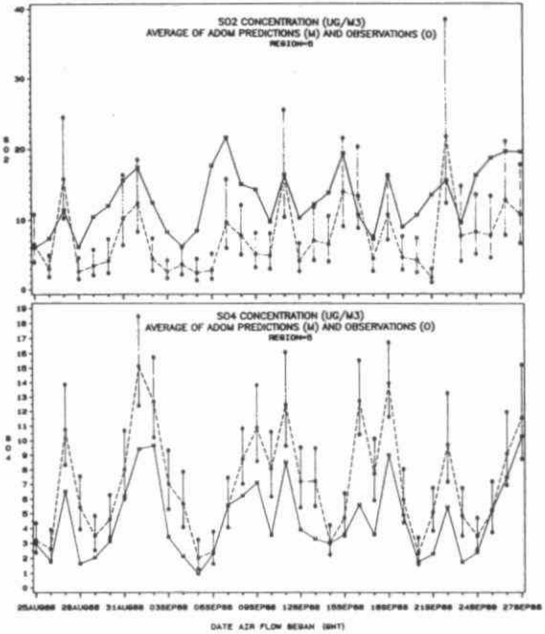

Figure 8. Time trends of ground level concentration for SO_2 and SO_4^{2-} during EMEFS.

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Modeling the influence of topography on dense gas dispersion

Stephen R. Ramsay*[1] & Rex E. Britter[2]

EnviroTech Research Limited
1386 Hastings Drive, London, Ontario N5X 1B1

1 Introduction

Topography, in the form of general slope, isolated hills, or more complex terrain, will alter or divert a dense gas cloud or plume. The topography may enhance plume dilution and divert the plume away from regions of elevated terrain; or, the dense plume may be channeled into valleys or low-lying areas and then be protected from the diluting influence of the ambient flow. These important effects are not included in the models currently used to predict the dispersion of a dense gas cloud for risk assessment or emergency management. The principal aim of this project is the development of numerical modeling techniques, based on rational physical principles, for incorporating the effect of topography in dense gas dispersion models.

This paper presents a review of some of the existing background theory and literature relevant to this problem. There is extensive treatment of the interaction of topography with buoyancy influenced flows in the geophysical literature, but little use has been made of this information source for dense gas dispersion. The report on which this paper is based (Ramsay & Britter 1990) provides a more extensive review of previous work on topographic effects on dense gas dispersion.

2 Gravity currents

The Front

The leading edge of a gravity current forms a frontal zone with a sharp interface between the dense fluid of the current and the surrounding ambient fluid. A characteristic 'head' which is deeper than the following flow is usually formed at the front. The raised head is a zone of breaking waves and intense mixing which plays an important role in the dynamics of the gravity current. A definition sketch for a gravity current is shown in Figure 1.

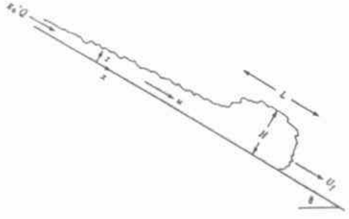

Figure 1: Definition sketch for gravity current.

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[1] also The University of Western Ontario

[2] also University of Cambridge

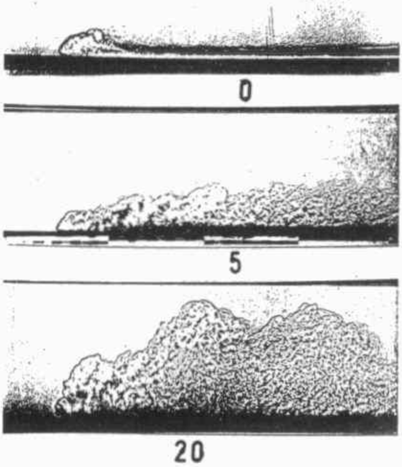

Figure 2: The effect of slope on the form a the gravity current head for slopes of 0°, 5° and 20° (from Britter & Linden 1980)

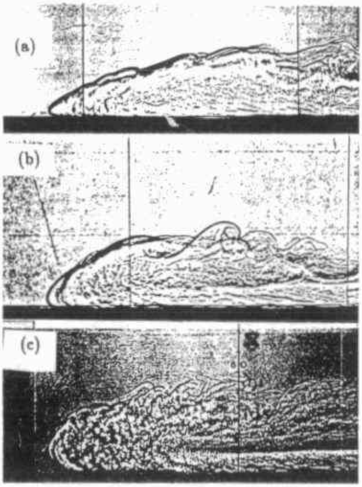

Figure 3: The effect of ambient flow on the form of the gravity current head (a) head wind (b) calm (c) tail wind (from Simpson 1987)

Gravity currents on slopes

A gravity current on a sloping surface is appreciably different from that on a horizontal surface. For a given rate of flow of a dense fluid on slopes of a few degrees to 90° slope there is a nearly constant front velocity. The front velocity is found to be about 60% of the mean velocity of the following flow. That is, about 40% of the flow arriving at the front is mixed into the head.

Figure 2 shows three different forms of the head of a gravity current: on a horizontal surface and on slopes of 5° and 20°, respectively. The head volume increases, both by direct entrainment and also by addition from the following flow. There is little variation of the front speed with slope because, although the gravitational forces increase with slope, so does the entrainment, both into the head and into the flow behind it.

Effect of ambient flow

The profile of the head of a gravity current and the velocity of the front are very sensitive to any opposing or following flow in the environment. These head- and tail-flow effects on the gravity current moving on a horizontal surface have been examined by Britter & Simpson (1978).

The experiments show that with a head wind the head profile is longer and the nose height lower than in the calm case previously described. With a tail wind the head is shorter and the node height is larger. The three different forms are shown in Figure 3.

3 Effect of slope

The classical analysis of Ellison & Turner (1959) is based on the theory of plumes with an entrainment function dependent on the overall stability characterized by an overall Richardson number. Several assumptions are made, the most important being: the turbulence is in a state of local equilibrium; the influence of the Reynolds number and the Prandtl or Schmidt number may be ignored; variations in density may be neglected in the inertial terms (i.e. the Boussinesq approximation); and, the pressure is hydrostatic normal to streamlines.

This flow is of considerable interest because it is a flow in which the density difference gives rise to both the flow down the slope and a reduction in entrainment through the density gradient strongly inhibiting turbulent mixing. That is, a flow in which the dynamics are self-limiting.

The characteristic plume velocity U and length h are defined by

$$Uh = \int_0^\infty U\,dy; \qquad U^2 h = \int_0^\infty U^2 dy \tag{1}$$

A scale for the local density difference $\Delta\rho$ is given by

$$g'Uh = g_0' q_0 = \text{constant} \tag{2}$$

where $g' = g(\Delta\rho/\rho_a)$ and q_0 is the volume flux per unit width at the source which has density difference $\Delta\rho = \rho_- \rho_a$ (the subscript 0 indicates conditions at the source). Thus the basic momentum equation is

$$\frac{d}{dx}(U^2 h) = -C_D U^2 - \frac{1}{2}\frac{d}{dx}(S_1 g' h^2 \cos\theta) + S_2 g' h \sin\theta \tag{3}$$

where the terms on the right are the surface shear, hydrostatic pressure and downslope gravitational acceleration, respectively, and

$$E = \frac{1}{U}\frac{d}{dx}(Uh) = \frac{U_e}{U} \tag{4}$$

The shape factors S_1 and S_2 are given by

$$S_1 g' h^2 = \int_0^\infty 2g\frac{\Delta\rho}{\rho_a} y\,dy; \qquad S_2 g' h = \int_0^\infty g\frac{\Delta\rho}{\rho_a} dy \tag{5}$$

and are typically 0.25 and 0.75, respectively. The surface shear stress is $\tau_0 = \rho C_D U^2$.

The entrainment function E is assumed to be a function of the overall Richardson number Ri

$$Ri = \frac{g'h}{U^2}\cos\theta = \frac{g_0' q_0}{U^3}\cos\theta \tag{6}$$

It was shown by Ellison & Turner (1959) that the general solution rapidly approaches the x−independent solution

$$E = \frac{dh}{dx} = \frac{S_2 Ri_n \tan\theta - C_D}{1.5 S_1 Ri_n} \tag{7}$$

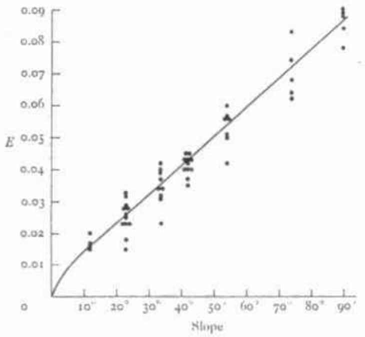

Figure 4: Measurements of entrainment into an inclined plume as a function of slope (from Ellison & Turner 1959).

where Ri_n is the x−independent solution of $Ri(x)$, and is termed the 'normal' Richardson number. That is, for any slope Ri_n is a constant and the velocity U is not a function of x but is proportional to $(g_0'q_0)^{\frac{1}{3}}$. It is immediately apparent from this equation that the behaviour of the inclined plume is independent of the wall stress at large slope. The rapidity with which the flow approaches the state at which $Ri = Ri_n$ suggests that the flow will also rapidly adjust to slope changes.

Further progress requires using experimental data which links two of E, Ri_n and θ. Although the $E - Ri$ correlation is more basic, the $E - \theta$ correlation is often used. These correlations have been the subject of much study and are central to the discussion which follows. There is still considerable doubt as to the correct correlations (see Delft Hydraulics Laboratory 1974).

4 Entrainment function

The experimental results on entrainment by Ellison & Turner (1959) may be approximated by $E \simeq 10^{-3}\theta$ for θ in degrees although data was only collected for angles greater than 10°. The variation of velocity (which is independent of x) with slope was from $1.5(g_0'q_0)^{\frac{1}{3}}$ at 10° to $2.15(g_0'q_0)^{\frac{1}{3}}$ at 90°. Pederson (1980) presents these entrainment results together with more extensive laboratory and field data and suggests $E = 1.2 \times 10^{-3}\theta$ for all angles greater than 6×10^{-3} degrees.

Entrainment at an interface appears to be determined by two distinct, yet not independent, mechanisms: the instability and subsequent mixing of the interface (i.e. a flow dependent on interface parameters; and, entrainment as a result of turbulence generated near the lower boundary propagating (diffusing) to the interface. The former is more relevant at large slopes while the latter only becomes significant for small slopes.

There is considerable evidence that a velocity/density interface is unstable when the gradient Richardson number is less than a critical value but stable above this critical value (see, for example, Sherman, Imbergher & Corcos 1978). With regard to the mixing as a result of turbulence generated at the interface it seems agreed (see Linden 1978) that the interface thickens until a limit is reached at which the interfacial Richardson number equals some critical value. The problem is more difficult when the mixing allows conditions on one or both sides of the interface to be altered by the mixing. The two dimensional plume on the slope falls into this category.

A further useful experiment is the free surface jet studied by Townsend (1957) and Ellison & Turner (1959). This experiment isolates entrainment due to interfacial instability from that due to boundary effects.

The basic equations for the continuous, steady, surface jet are:

$$\frac{1}{U}\frac{d(Uh)}{dx} = E \tag{8}$$

and

$$\frac{d(U^2h)}{dx} + \frac{1}{2}\frac{d(S_1 g' h^2)}{dx} = 0 \tag{9}$$

which integrates to

$$U^2h + \frac{1}{2}S_1 g' h^2 = \text{constant} \neq f(x) \tag{10}$$

This can be written as

$$\frac{h(1 + .5S_1 Ri)}{Ri^{\frac{2}{3}}} = \text{constant} \neq f(x) \tag{11}$$

From these experiments Ellison & Turner (1959) were able to deduce the variation of E with the Richardson number. E decreased from about 0.075 at $Ri \simeq 0$ to zero at a critical Richardson number of about 0.8. Koh (1971) supports this result and suggests the empirical form

$$E = 0.075\left[2\left(1 + \frac{Ri}{0.85}\right)^{-1} - 1\right]^{1.75} \tag{12}$$

Longuett-Higgins & Turner (1974) use the form

$$E = \frac{0.08 - 0.1Ri}{1 + 5Ri} \tag{13}$$

The other source of mixing is from turbulence generated away from the interface. The simplest and most common example of this would be where the turbulence is generated by the shear at a nearby rigid boundary. Dimensional analysis would suggest that

$$E = \frac{U_e}{U} = f\left(\frac{g'h}{U^2}\right) \tag{14}$$

where g' characterizes the density difference across the interface, and h characterizes either the distance from the boundary to the interface or the scale of the turbulence.

Lofquist (1969) studied the entrainment rates into flowing underlayers under conditions where interfacial instability is small. The literature survey carried out by the Delft Hydraulic Laboratory (1974) fitted Lofquist's data with

$$\frac{U_e}{U} \simeq 10^{-3}\frac{U^2}{g'h} \simeq 10^{-3}Ri^{-1} \tag{15}$$

although a coefficient of 5×10^{-4} is as good a fit to the data. At large Richardson number, Hansen (1975) and Hamblin & Carmack (1978) suggest that $U/U_e \simeq 2 \times 10^{-3}Ri^{-1}$, a result similar to Lofquist's.

Large scale data are rare but Hebbert *et al* (1979) supply information from a density inflow into the Wellington reservoir. They estimate $E = U_e/U \simeq 1.9 \times 10^{-4}$ when $Ri \simeq 17.4$. A coefficient of 2 in the above equation requires $C_D \simeq 0.014$, which is not an unrealistic value. Note that the use of $E \simeq 1.2 \times 10^{-3}\theta$ gives (with $\theta \simeq 0.06°$) $E \simeq 7.4 \times 10^{-5}$.

When Ri_n is very large and interfacial instability is weak, or zero, several authors argue that the result should be correlated in the form $E \propto Ri_n^{-1}C_D^{\frac{3}{2}}$ bringing out the explicit dependence on the wall shear stress.

Fischer *et al* (1979) argue that when the shear production is negligible ($Ri > 0.8$) then

$$E = CC_D^{\frac{3}{2}}\frac{U^2}{g'h} \tag{16}$$

That is

$$E = CC_D^{\frac{3}{2}}Ri_n^{-1} \tag{17}$$

with $C = 3.2$ given by the field experiments of Elder & Wurderlich (1972) and Hebbert *et al* (1979).

Lofquist (1969) gave $(u_*/U)^2 \simeq 5 \times 10^{-3}$ for his experiments. That is,

$$\frac{U_e}{U} \simeq 0.10\left(\frac{g'h}{u_*^2}\right)^{-1} \tag{18}$$

or

$$\frac{U_e}{u_*} \simeq 1.4\left(\frac{g'h}{u_*^2}\right)^{-1} \tag{19}$$

Thus

$$E = 1.4C_D^{\frac{3}{2}}Ri_n^{-1} \tag{20}$$

Kato & Phillips (1969) and Kantha, Phillips & Azad (1977) studied a constant stress experiment and found coefficients of 2.5 and 5.0 in two different experiments, the first using a continuous stratification and the second a two-layer density stratification, the coefficients referring to the correlation $U_e/u_* \propto (g'h/u_*^2)^{-1}$

Although there is still uncertainty about the relevant entrainment function, we assume that E is a known function of C_D and Ri in the following discussion. For example, Figure 5 suggests a typical combination of $E - Ri$ using the Ellison & Turner surface jet results at small Ri_n and $E \propto C_D^{\frac{3}{2}}Ri_n^{-1}$ at $Ri > 1$.

A final cautionary note is required ont he correlation of E with $C_D^{\frac{3}{2}}Ri_n^{-1}$. It is often uncertain as to what C_D is meant to represent. Typically C_D is the drag coefficient $(u_*/U)^2$ for a particular surface with non-stratified flow. However, it may be easily shown that $C_D = f(Ri)$, although this dependence is normally neglected. Carson & Richards (1978) estimate that for the atmospheric boundary layer C_D is no larger than 3×10^{-4}

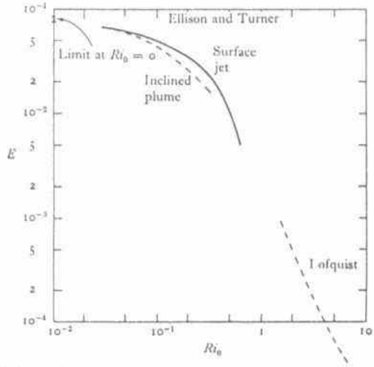

Figure 5: Rate of entrainment into a turbulent stratified flow as function of overall Richardson number (from experiments of Ellsion & Turner (1959) and Lofquist (1960).

regardless of surface roughness for $Ri > 0.3$. Little difficulty arises provided all correlations are based on what C_D would be for the same mean velocity but $Ri = 0$.

The drag coefficient C_D includes the shear stress at the rigid surface and the (non-entraining) shear stress at the interface. The interfacial shear stress is small and negligible compared with the shear stress at the surface (Delft Hydraulic Laboratory 1974).

5 Effect of ambient flow

Ellison & Turner (1959) considered theoretically the interaction of a two-dimensional line source on a slope with a moving ambient up or down a slope. Their analysis is limited to cases where: the moving ambient is non-turbulent; and, the ambient either opposes the buoyancy driven motion or the ambient flow is smaller than the buoyancy driven flow when they are in the same direction. When the ambient fluid is dragging the plume forward Ellison & Turner (1959) argue that the entrainment may have a different dependence on Ri.

If U is the plume velocity relative to the ambient velocity U_a then

$$g'(U + U_a)h = g_0'q_0 = \text{constant} \tag{21}$$

$$\frac{dh(U + u_a)}{dx} = E|U| \tag{22}$$

$$E = f(Ri) = \frac{g_0' q_0 \cos\theta}{U^2(U + U_a)} \tag{23}$$

and

$$\frac{d}{dx}\left[(U + U_a)Uh\right] = -(U + U_a)^2 C_D \text{sgn}(U + U_a) + S_2 g' h \sin\theta - \frac{1}{2}\frac{d}{dx} g' h^2 S_1 \cos\theta \tag{24}$$

Arguing that the flow rapidly adopts a 'normal' state in which

$$\left(1+\frac{1}{2}S_1 Ri\frac{U}{U+U_a}\right)E = S_2 Ri\tan\theta - C_D\frac{(U+U_a)^2}{U^2}\mathrm{sgn}(U+U_a) \tag{25}$$

Ellison & Turner (1959) obtain numerical solutions for the plume velocity $(U+U_a)/(g_0'q_0)^{\frac{1}{3}}$ as a function of $U_a/(g_0'q_0)^{\frac{1}{3}}$ (Figure 6). It is useful to note that the relevance of U_a may be determined by comparing it with $A = g_0'q_0$.

The curves in Figure 6 could be simply obtained by further numerical computation for other slopes and C_D, however, some of the limits are useful and easily obtained.

When $C_D = 0$ then

$$\left(1+\frac{1}{2}S_1 Ri\frac{U}{U+U_a}\right)E = S_2 Ri\tan\theta \tag{26}$$

If U and U_a are in the same direction and the slope is not very small $1+\frac{1}{2}S_1 Ri\frac{U}{U+U_a} \ll 1$ and, thus, $Ri = \frac{E}{S_2\tan\theta}$. This solution is such that the ambient velocity is simply added to the plume velocity in the absence of the ambient flow. A similar result holds when the ambient flow opposes the buoyant velocity. Dilution of the plume is reduced by a factor $\frac{U}{U+U_a}$ in the former case and enhanced by $\frac{U}{U+U_a}$ in the latter case.

A further particularly useful result is the ambient velocity required to reverse the buoyant flow of the plume. This is only a weak function of C_D and typically $U_a/(g_0'q_0)^{\frac{1}{3}} \sim 3-4$ increasing with slope.

Britter (1980) estimates that an ambient flow much greater than twice the leading edge velocity will stop the motion of the cloud. As the downslope velocities are not greatly enhanced by an increased slope, the upwind ambient velocity required to reverse the cloud is not greatly affected by the slope. This argument is consistent with Ellison & Turner's (1959) calculations and experiments.

No calculations or systematic experiments are available for anything other than the simple two-dimensional line source on a constant slope, however they may be obtained subject to the previous assumptions.

For a point or area continuous source it can be argued, without recourse to analysis, that the plume will not travel further against the ambient whenever $U_a/(g_0'\frac{Q_0}{w})^{\frac{1}{3}}$ exceeds 3-4 where w is the local width of the plume. This would seem to be a useful criterion for determination of the upwind distance that a plume might travel.

For the instantaneous source a similar argument would suggest that the cloud will not travel against the ambient flow unless, in the absence of the ambient flow, its velocity is more than about twice that of the ambient velocity.

Note also that significant upwind (downslope) travel is possible if the material does not spread laterally (e.g. if it is channeled into a small valley).

6 Conclusions

Topographic features that are small compared with the size of the release may be considered in much the same way as buildings or structures but without any substantial flow separation unless the topography is very abrupt. The shallow water equations are useful here (Lamb & Britter 1984, Lee & Meroney 1988). When the topographic feature is large compared with the scale of the release, the topography reduces to the

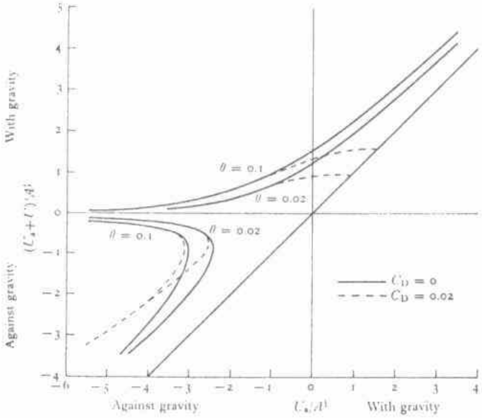

Figure 6: Calculations of the velocity of an inclined plume entraining a moving ambient flow (from Ellison & Turner 1959).

local slope. Somewhat surprisingly, the downslope velocity of a dense fluid released on a slope under calm conditions is not a strong function of the slope.

Broadly, three characteristic velocities are relevant: the ambient wind velocity; the buoyancy generated velocity found on flat terrain; and, the buoyancy generated velocity found on slopes (downslope). The latter two velocities both scale on $(g'h)^{\frac{1}{2}}$. As the coefficient in the expression for the slope flow is only a weak function of slope, the slope will have an effect on the clouds for which any buoyancy generated velocities are relevant. However, the flow development times may differ. For example, the instantaneous release might initially spread radially, then develop a bulk downslope flow, before finally being diluted and swept upslope by an ambient flow.

When the wind is upslope, the cloud widens and its dilution is enhanced. When the wind is downslope, the cloud is narrower and the dilution is decreased. The variation of the lateral growth of the plume results from the effective summation of the wind and the buoyancy induced motion down the slope. The entrainment is influenced by the velocity shear and will therefore be enhanced by an upslope wind and reduced by a downslope wind.

A distinctly different topographic influence occurs when the topography alters the velocity field within the cloud which is dispersing. Britter & Snyder (1988) found this to be more important than the direct effect of the slope on the cloud.

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A8

IGNITION STUDIES OF SELECTED EXPLOSIVE MIXTURES OF GASES AND DUSTS EMITTED FROM CEMENT KILNS

Authors

I.I. Inculet*, G.S.P. Castle*, E.J. Weckman**, K.A. Shelstad* and M.L. Wick*

* I.I. Inculet, G.S.P. Castle, M.L. Wick, Electrical Engineering; K.A. Shelstad, Chemical Engineering; The University of Western Ontario, London, Ontario, Canada N6A 5B9

** E.J. Weckman, Mechanical Engineering; The University of Waterloo, Ontario, Canada N2L 3G1

Abstract: The gas compositions and the dust loadings of two cement plants were investigated. The samples were taken at the inlet and the outlet of the electrostatic precipitators and then analyzed on a gas chromatograph. The measured gas concentrations were used as a basis for flammability tests in order to verify or correct existing safe operation limits for the precipitators.

Two sets of flammability tests were conducted using a modified version of the 20 litre chamber designed by the U.S. Bureau of Mines. In the first set the lean limits of different clean gas mixtures which are assumed to be present under upset operating conditions were determined. In the second set the amount of cement dust necessary to render an explosive clean gas mixture inert was examined.

The results of the flammability tests showed that the measured exhaust gas composition was well in the safe range. Under upset conditions however, the gas composition could be explosive and in most cases the amount of dust present in the precipitator exhaust gas would not be sufficient to prevent an ignition of the gas.

I. INTRODUCTION

The operation of cement plants generates a considerable amount of cement dust which generally is collected by means of electrostatic precipitators (ESP). Inside the cement kilns, the calcination process is accompanied by the formation of carbon monoxide, hydrocarbons and other combustible gases. During transient conditions of the process, these gases may form explosive mixtures which could be ignited by the high energy sparks in the ESP. To prevent such hazardous conditions to develop, the kiln emissions of carbon monoxide and oxygen are continuously monitored by the cement industry. If an impending or already formed explosive mixture is detected, the electrostatic precipitators are immediately de-energized to prevent any sparks. The decision to shut down the precipitators, currently, is premised on very safe limits for allowable concentrations of combustible gas, without taking into account the unknown influence of substantial concentrations of cement dust present in the kiln exhaust gas. The scope of the investigation was to define new safety limits to minimize the number and duration of the power-outs of the precipitators. The paper includes analyses of actual exhaust gas samples from cement kilns and results from flammability test conducted on representative clean gas mixtures and various gas-cement dust mixtures.

II. COMPOSITION OF CEMENT KILN EXHAUST GAS

Kiln exhaust gas and dust loading samples were collected at two cement plants, each running different process streams. Two sets of 12 samples each were collected at various times at both the inlets and the outlets of the electrostatic precipitators. Each sample was analyzed for its gas composition using a gas chromatograph.

The dust loading was measured using thimble filters in which the dust was collected for a specified time period. Table 1 shows a summary of the average gas compositions and dust concentrations. In all cases, the variation of the gas concentrations was within 7% of the mean. No test was conducted under upset conditions in the process stream, so the found results provide a good indication of the background gas concentrations and the dust loadings under normal operating conditions. The results compared well with reference values estimated by the plant personnel.

Table 1: Kiln exhaust gas composition and dust loadings

Sample #	Position	CO_2	O_2	N_2	CO	H_2	UBHC	Dust loading [g/m³]
Plant 1, A	Inlet	28.5	3.6	64.7	0.13	< 0.02	< 0.06	32.7
Plant 1, A	Outlet	26.0	4.8	63.6	0.098	N/D	N/D	6.7
Plant 1, B	Inlet	21.4	7.4	N/D	0.15	N/D	N/D	not taken
Plant 1, B	Outlet	not taken						
Plant 2, A	Inlet	24.0	6.1	61.0	0.011	N/D	N/D	514.1
Plant 2, A	Outlet	23.1	6.5	63.3	0.014	N/D	N/D	< 15.0
Plant 2, B	Inlet	24.9	6.1	63.4	0.034	N/D	N/D	573.2
Plant 2, B	Outlet	24.6	6.4	63.9	0.021	N/D	N/D	< 2.0

The results in Table 1 indicate that the exhaust gas of both cement plants contain typically 25% CO_2 and 63% N_2 at either inlet and outlet of the precipitator. The concentration of CO varied considerably from 0.1% in Plant 1 to 0.03% in Plant 2. Concentrations of H_2 and unburned hydrocarbons (UBHC), the latter one mainly composed of methane, exhibited some variability with time, but were present only in very small concentrations under normal operating conditions. In Plant 2, the O_2 concentration was typically 6%, but in Plant 1 it changed from 4-7.5% between samples A and B. This was due to substantial modifications in the process stream so sample B is thought to be most representative for normal operating conditions in Plant 1. A comparison with published explosion limits for single gases indicated that a mixture containing any one of the flammable gases at these concentrations would not ignite in the electrostatic precipitator [1].

Representative dust loadings, as shown in Table 1, lie in the range from 30-550 g/m³. The literature suggests that for volatile dusts, dust-air mixtures with loadings of 100 g/m³ could ignite under certain conditions, while loadings of 10-80% inert dust could suppress explosion even for very high ignition energies [2]. Thus, it was decided to test the full rage of dust loadings measured in the cement plant kiln exhaust and to extend the range depending on the initial results.

III. FLAMMABILITY TESTS OF KILN EXHAUST GASES

A. The Experimental Apparatus

The experimental apparatus used to test the flammability of representative clean gas and gas-dust mixtures is shown schematically in Figure 1. It was comprised of the explosion chamber, the associated gas handling system, a spark generating apparatus to ignite the gas and two transducers to detect an explosion. The chosen explosion chamber was a modified version of the 20 litre test chamber designed by the U.S. Bureau of Mines [3], shown in detail in Figure 2. Its volume was 25.5 litres. The original chamber has been shown to produce repeatable measurements of minimum ignition energies for gases, dusts and gas-dust mixtures [2,3].

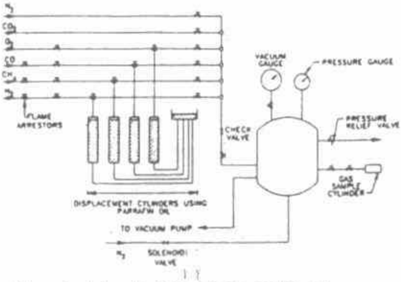

Figure 1: Schematic of the explosion chamber and associated gas handling system

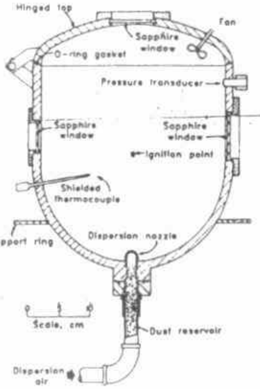

Figure 2: Details of the explosion chamber showing the instrumentation

The gas-dust mixture was ignited by means of a custom electric spark apparatus, consisting of a high voltage power supply and a variable capacitor unit. First the capacitor was charged to the appropriate voltage and then discharged between two sharp needle points to generate the spark.

To detect an explosion, the test chamber was equipped with a pressure transducer and a shielded thermocouple which were connected to a storage oscilloscope.

For each test, the chamber was evacuated, then purged with N_2, evacuated again and filled with the inert gases by partial pressure and the flammable gases by using displacement columns. Thorough mixing was accomplished by the filling procedure and was further enhanced using a fan inside the chamber. The final gas compositions were cross-checked using a batch gas sample that was analyzed on the gas chromatograph. No major discrepancies between the target and achieved gas compositions were noted.

1) Characterization Of The Apparatus: The operation of the explosion chamber was tested by running a series of explosions using H_2/air mixtures with N_2 as the diluent. It was found that explosions occurred for H_2 concentrations greater than 6% and less than 32% with O_2 concentrations of 7% and 6% respectively. These values correspond well with those found in the literature [1], indicating that the explosion vessel was operating correctly.

B. Flammability Of Gas Mixtures Without Dust

Two separate sets of flammability tests with clean gas mixtures were carried out. The initial one was used to determine wether the typical exhaust gas in the precipitator was explosive or not. No one of the gas compositions listed in Table 1 ignited, even with spark energies of 3-5 J. This was expected since, under normal operating conditions, the probability of an explosion in the cement plant is very low.

The danger in operation occurs when the process undergoes an upset in conditions since transients might increase the concentrations of flammable gases by as much as 50 times. This would increase the concentrations of CO to 7.5%, of H_2 to 1% and of CH_4 to 3%. It was not known whether this mixture would explode, since the flammability limits for many multiple gas mixtures have not been recorded previously. To test the flammability limits of gas mixtures similar to those postulated for upset conditions, a composition of 25% CO_2, 8% O_2 and 1.5% CH_4 was chosen as a base mixture. The quantities of CO, H_2 and N_2 in the mixture were varied individually and in combination to find the lean flammability limits. For a mixture as above but also containing 2.5% CO, the amount of H_2 was increased form 0.1% to greater than 30% (with corresponding decreased in the quantity of N_2). In no case did the gas mixture explode. A second mixture as above, but with 1% H_2 was used to test varying proportions of CO and N_2. It was found that explosions occurred for mixtures containing greater than 10% CO. When the percentage of H_2 was increased to 3%, explosions occurred in mixtures with only 7.5% CO. The results are shown with other published data in Figure 3. The agreement is good and clearly indicates the sensitivity of flammability limits to concentrations of all flammable gases, particularly when they are found combined in a mixture.

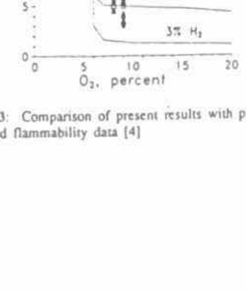

Figure 3: Comparison of present results with previously published flammability data [4]

C. Flammability Of Gas-Dust Mixtures

The next series of experiments were conceived to test the flammability of gas-dust mixtures which were assumed to represent the kiln exhaust under upset operating conditions. In the four cases studied the concentration CO_2 and CH_4 was held constant at 25% and 1.5% respectively. The concentration of O_2 and H_2 was changed for each case to investigate the noticed sensitivity of explosions towards these gases, and the amount of CO was varied to find the flammability limits. The N_2 was used to fill to make 100% mixture.

Once the lean limit was found for each case, the quantity of cement dust required to inert an explosive gas mixture was determined for incrementing CO levels. The type of cement dust was the same for all flammability tests described below. Its mean particle diameter was 4 µm with the 10% limit at 2 µm and the 90% limit at 12 µm.

1) Case 1: 8% O_2 and 1.5% H_2: In the first set of flammability tests with clean gas and gas-dust mixtures a base gas consisting of 25% CO_2, 8% O_2, 1.5% CH_4 and 1.5% H_2 was used. The amount of CO was varied and N_2 was added to make 100% mixture. The results of the tests are plotted in Figure 14 as concentration of CO in the clean gas mixture versus concentration of cement dust added to the mixture.

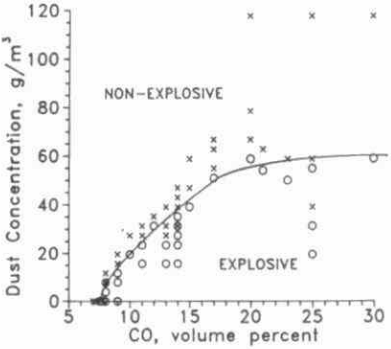

Figure 4: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 8% O_2, 1.5% CH_4, 1.5% H_2

The clean base gas exploded for CO concentrations greater than 7.5%, as can be seen from Figure 5. This is consistent with results obtained previously. For increasing concentrations of CO in the base gas mixture, it took increasing quantities of cement dust to render the gas mixture non-explosive, up to concentrations of approximately 17% CO. At this concentration of CO it took approximately 50 g/m³ of cement dust to suppress an explosion.

For concentrations of CO greater than 17%, an asymptotic limit appeared to had been reached where no more than 50 to 60 g/m³ cement dust was required to suppress an explosion up to concentrations of CO as high as 30%.

These results suggest that if the cement dust concentration was maintained above the apparent asymptote of 50 to 60 g/m³, the danger of an explosion in the cement plant precipitators could be reduced. Unfortunately, while this dust concentration is below the level measured at the inlet to the precipitators in Plant 2, it is substantially higher than the dust concentrations measured at the outlet to Plant 2 or at the inlet or outlet in Plant 1. Therefore, it can not be expected that the presence of the cement dust in the process stream would always render explosive mixtures of gases inert when the plant is operating under upset conditions.

2) Case 2: 8% O_2 and 3.0% H_2: The second set of flammability tests with clean gas and gas-dust mixtures was carried out using a base gas composed of 25% CO_2, 8% O_2, 1.5% CH_4 and 3.0% H_2. The amount of CO was varied and N_2 was added to make 100% mixture. The results of the tests are plotted in Figure 5 as the concentration of CO in the gas mixture versus the amount of cement dust dispersed in the gas mixture.

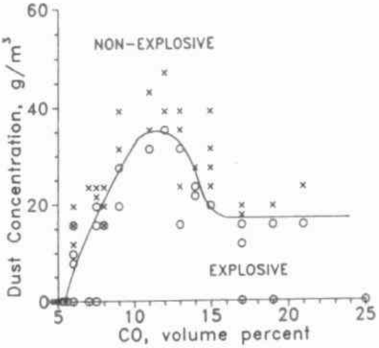

Figure 5: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 8% O_2, 1.5% CH_4, 3% H_2

Figure 5 shows that the clean base gas exploded for CO concentrations greater than 5%. In the range of 5% to approximately 12% CO, increasing quantities of cement dust were necessary to render the gas mixture non-explosive for increasing concentrations of CO. At the upper end of the range it took approximately 35 g/m³ of cement dust to suppress an explosion. For concentrations of CO greater than 12%, the quantity of dust required to suppress an explosion decreased sharply, reaching an asymptotic limit of 15-20 g/m³ for concentrations of CO greater than 16-17%.

Through comparison of Figure 4 and Figure 5 it can be seen that doubling the quantity of H_2 in the base gas (Case 2) increased the flammability of the clean gas mixture since it required CO concentrations of only 5% to cause an explosion in Case 2. In similar fashion to Case 1, it took increasing quantities of cement dust to render the mixture inert for increasing concentrations of CO. However, for the same concentrations of CO as in Case 1, it generally took more dust to suppress an explosion for the base gas used in Case 2. This suggests that increases in the quantity of H_2 in the base gas lead to explosions that are more difficult to suppress with the cement dust.

In sharp contrast to the results in Case 1, for Case 2 it appeared that with CO concentrations greater than 12%, the quantity of dust required to suppress explosion sharply decreased, reaching an asymptotic value much lower than that observed in Case 1. These trends and the value of the limit were completely unexpected, and may be due to scatter in the data resulting from the small number of verification tests performed at these high CO concentrations.

3) Case 3: 9% O_2 and 1.5% H_2: Since the explosion tests of the clean gas mixtures showed a high sensitivity towards the O_2 concentration, further tests were conducted on gas and gas-dust mixtures using a base gas composed of 25% CO_2, 9% O_2, 1.5% CH_4 and 1.5% H_2. The amount of CO was varied and N_2 added to make a 100% mixture. The results are plotted in Figure 6 with the CO concentration versus the quantity of cement dust added to the gas mixture.

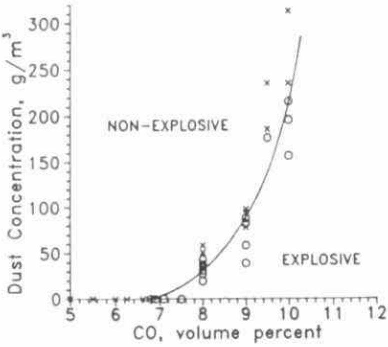

Figure 6: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 9% O_2, 1.5% CH_4, 1.5% H_2

It can be seen from Figure 6 that the clean base gas exploded for CO concentrations greater than 6.5%. For increasing concentrations of CO in the base gas mixture, it took greatly increased quantities of cement dust to render the gas mixture non-explosive. The results appeared to have an exponential rather than an asymptotic behaviour. This might have been due to the fact that the dust dispersion mechanism of the experimental apparatus did not operate repeatably for cement dust loadings greater than 350 g/m^3 and a possible asymptotic region could not be reached.

A comparison of Case 1 and Case 3 indicates that if the content of O_2 in the base gas is increased from 8% to 9%, the quantity of cement dust required to suppress an explosion rises by approximately a fivefold for similar concentrations of CO. All the quantities of dust required to suppress explosions in Case 3 are well above the concentrations that were measured at the inlet or outlet of cement Plant 1 or at the outlet of Plant 2 and, when a concentration of 10% CO is reached, they are approaching those measured at the inlet of Plant 2.

4) Case 4: 9% O_2 and 3.0% H_2: The final set of tests was conducted on gas and gas-dust mixtures using a base gas of 25% CO_2, 9% O_2, 1.5% CH_4 and 3.0% H_2. Like for the previous tests, the amount of CO was varied and N_2 added to make 100% mixture. The results are plotted in Figure 7 as concentration of CO in the gas mixture versus amount of cement dust dispersed in the gas mixture.

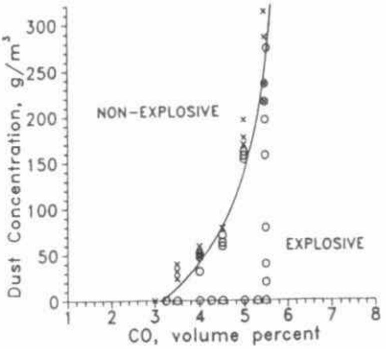

Figure 7: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 9% O_2, 1.5% CH_4, 3% H_2

From Figure 7, it is evident that the clean base gas exploded for CO concentrations greater than 3.0%. As in Case 3, for increasing concentrations of CO in the base gas mixture, it took greatly increased quantities of cement dust to render the gas mixture non-explosive. The curve is even steeper than the one in Case 3, as would be expected with the higher concentrations of H_2 present in the base gas. For a set of tests not shown, with concentrations of 7.5% CO, it was not possible to suppress explosion, even with dust loadings greater than 300 g/m^3. No asymptote was apparent in the results of Case 4.

A comparison of Case 2 and Case 4 indicates that, for similar concentrations of CO, a 1% increase in O_2 concentration provides a mixture in which explosion cannot be suppressed, even with very large quantities of cement dust. The concentrations of cement dust which would be required to suppress explosion in mixtures containing even the lowest concentrations of CO found in these base gas mixtures are much higher than those measured at either the inlets or the outlets of the precipitators in Plants 1 and 2. With 9% concentration of O_2 in the base gas, then, the danger of explosion is very real, even for modest quantities of CO in the precipitator gases.

5) Observations: In all of the cases discussed above, only one type of cement dust has been used to determine the concentrations of dust required to suppress explosion in the base gas mixtures. It has been reported that results in flammability testing of gas-dust mixtures are dependent on both the composition and particle size of the dusts used in the experiments. In addition, the uniformity of dust concentration in gas-dust mixtures has been shown to influence flammability results.

In a independent set of tests, the effects of cement dust particle size on explosion suppression were tested by passing the dust through a fine sieve before dispersing it in the explosion chamber. Subsequently, it was found that 10-15% less dust was required to suppress explosion in a given gas mixture. The results should serve as a warning that the absolute concentrations given in this report are not universal limits on the quantities of cement dust that would be required to render an explosive gas mixture inert.

IV. CONCLUSIONS

1. Analysis of samples of kiln exhaust gases collected at Plants 1 and 2 indicated that, under normal operating conditions, the concentrations of flammable gases in the exhaust are well below those required to form an explosive mixture.

2. Under plant upset conditions, it is conceivable that explosive gas mixtures might be formed. Flammability tests of simulated exhaust gas mixtures without dust indicated that, while the explosion limits are very sensitive to the concentrations of CO and H_2 in the mixture, they are far more dependent on the O_2 concentration in the background gas.

3. Flammability tests of gas-dust mixtures with a single type of dust indicated that with 8% O_2 in the base gas, 50 g/m^3 of cement dust appeared always to render an explosive gas mixture inert, even when the CO concentration exceeded 20%. Unfortunately, this dust loading is higher than those normally encountered in the cement plant precipitators. Therefore, the presence of cement dust in the process stream should not be expected to suppress explosion in the precipitators when the plant is operating under upset conditions.

4. In all flammability tests, increasing quantities of H_2 in the base gas led to more explosive mixtures. Therefore, greater quantities of cement dust were required to suppress explosion in mixtures containing higher concentrations of H_2.

5. When the O_2 concentration in the base gas was increased from 8% to 9%, the flammability behaviour changed drastically. For small increases in CO concentration in the base gas, exponential increases occurred in the quantity of dust required to suppress explosion. If levels of 9% O_2 were ever reached in the kiln exhaust gases, the danger of explosion in the precipitator would be greatly increased, even with levels of CO as low as 5-7% by volume.

6. A series of short tests showed that the results obtained are dependant on the type and the size distribution of the cement dust and therefore the results of the tests must be applied with care.

7. In general, it takes high loadings of cement dust to effectively suppress explosion in a mixture of flammable gases that might be found in the cement kiln exhaust gases. Therefore, the presence of dust in the exhaust gas stream should not be expected to render an explosive gas mixture inert, particularly, for instance, at the precipitator outlet where the dust loading is usually quite small.

8. Since the flammability of the gases appeared to be more sensitive to CO and H_2 concentration than to that of UBHC (CH_4), monitoring the concentrations of these gases should remain a major part of the plant control operation.

9. The flammability of typical exhaust gas mixtures is highly dependent on the concentration of O_2 in the mixture, therefore the danger of explosion might be reduced by maintaining the exhaust gas O_2 concentration below about 6-7%, i.e., by minimizing leakage in the region of the precipitators.

10. If more detailed information was available on the upset conditions that occur in a specific cement plant, the results of this study might be more meaningfully interpreted for analyzing the possible explosion hazard.

VI. ACKNOWLEDGEMENTS

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A9

EVALUATION OF METHODS TO DETERMINE THE IMPACTS OF RESIDENTIAL WOODBURNING ON AMBIENT AIR IN ONTARIO

M.E. Yandle, C.S. Davis, D.L. Dougherty

Abstract

During the fossil fuel shortage of the mid seventies, the availability of fuel wood prompted a significant increase in the use of residential wood stoves and fireplaces in many North American and Scandinavian communities. In Ontario, an increasing number of residents have been using wood stoves to substitute or augment heating provided by other means, as well as using wood burning fireplaces.

The increased use of residential wood as a fuel has resulted in deterioration of ambient and indoor air quality is several areas. The most direct evidence of this deterioration has been the increase in ambient total suspended particulate and carbon monoxide levels especially in areas that have poor atmospheric dispersion conditions. The concern over the air quality impact of residential wood combustion (RWC) is heightened by the composition of the emissions which have proven to contain toxic and carcinogenic species of which the polynuclear aromatic (PNA) compounds are most important. The PNA compounds emitted may undergo atmospheric chemical reactions with nitrogen oxides and ozone to produce a further variety of compounds which are potentially toxic or mutagenic.

Investigation in the United States of areas of non-attainment of carbon monoxide (CO) and aerosols revealed the significant impact of the collective effect of residential wood combustion (RWC). Special studies to determine the air quality impacts of RWC were undertaken in several wood-burning states especially in the Pacific Northwest - Colorado, Washington, Oregon, Idaho, as well as in states such as Minnesota, Michigan, New York, Maine, North Carolina, New Hampshire and Vermont. As can be anticipated, results of these studies confirmed the necessity to adopt standards of stove efficiency. To complement these efforts, the emissions produced by woodstoves were investigated. Areas examined included: chemical composition, emission rates, and physical factors affecting the combustion process (moisture content, stove efficiency, etc.).

In Ontario, complaints regarding RWC emissions have been registered with municipal and regional government offices. The Ontario Ministry of the Environment has recognised the significance of the RWC sources in several communities and a study to investigate the potential impact of RWC sources on ambient air quality was undertaken by Concord.

The first phase of the study has reviewed and compiled current information regarding the environmental impact of residential wood combustion. In the future, areas of significant potential for adverse air quality impacts from RWC in Ontario will be studied in order to characterize the extent of the impacts and to determine the need for appropriate control and abatement policies and strategies.

Objectives

The objectives of the first phase were to search the relevant literature, review articles and reports, and to summarise the current status on the following topics:

- current emission regulations and abatement strategies;
- source characterization;
- sampling techniques;

- analytical techniques;
- airshed impact studies;
- atmospheric (chemical and phase stability); and
- data analysis and assessment methods (tracer methods, chemical mass balance, receptor modelling, multivariate methods, etc.).

The focus of this study was to gather relevant information and evaluate the technical merits of the past research efforts and to assess the potential for RWC impacts in Ontario and to recommend further action. The recommendations were based on an experimental design that will incorporate the most effective sampling and analytical methods to collect the optimum amount of information required to assess the RWC impacts and, where necessary, resolve contributions from similar sources. The intent of a subsequent investigation will be to quantify and document the effects of RWC in selected areas in Ontario.

Methodology

The relevant literature databases were searched and the pertinent articles and reports were obtained. The information was categorized into the areas of interest and was reviewed in the context of the objectives. Invariably, some documents impinged upon several topics, and articles of this nature were reviewed successively. The approach of the literature review was to provide a concise, focused evaluation of current technology, rather than an article by article review.

Review of Controls and Regulatory Strategies

Wood heating appliances are regulated by a wide variety of programs and provisions that either directly or indirectly impact upon the design, testing, performance and installation of the appliance with respect to air contaminant emissions. In several areas of the United States especially in the northwest, the increased use of residential wood heating appliances has forced many areas to develop and implement measures designed to regulate the amount of emissions produced by woodstoves. The measures fall into three categories:

1. the development of efficiency, design and emission codes and standards for wood burning appliances;
2. setting maximum permissible air pollution levels and installation regulations; and
3. control strategies and programs and non-regulatory activities.

Regulations promulgated have included:

- design and/or technology standards (woodstove certification requirements);
- emission standards for particulates, and in some cases carbon monoxide and/or opacity;
- voluntary and mandatory burning curtailment on days of poor air quality; and
- limitation of the number of installations.

Control strategies and programs vary and typically include one or more of the following elements:

- public education programs;
- voluntary burning curtailment;
- woodstove retrofits (with catalytic converters);
- certified woodstove replacements;

- firewood seasoning rules;
- weatherization of wood-heated homes;
- wood stove licensing; and
- incentive programs such as low interest or no interest loans, tax credits, preferred utility rates, rebates, etc. for replacement and or upgrading of units.

In early 1984, the Canadian Standards Association assembled a Committee to develop a comprehensive performance test standard for wood stoves. The Canadian Wood Energy Institute and the Department of Energy, Mines and Resources (EMR) triggered the formation of the Committee. Its mandate was two-fold: firstly, to develop test procedures designed to provide reproducible performance measures, and secondly, to assess whether performance testing should be voluntary or mandatory, and whether pass/fail criteria should be established.

The preliminary standard was developed and incorporated specific guidelines regarding test facilities, instrumentation, fuelling methods, testing procedures and, finally, the manner in which test results would be calculated for such key indicators as heat output, average stack temperature, burn time (duration of burn), appliance efficiency and emissions (Braaten, 1984). The preliminary standard however did not incorporate maximum emission nor minimum efficiency standards and was never promulgated. The Committee is currently revising the standard to incorporate both maximum emissions and minimum efficiency standards similar to U.S. EPA federal standards. A draft form of the revised standard was to be ready during the next Committee meeting in February 1990 (B. Wier, 1989). Some effort has been made by the Committee to harmonize development of the CSA standard with EPA.

Factors and Effects on Emissions

In all combustion processes, both physical and chemical factors (variables) affect the efficiency of combustion and also the emissions produced by the combustion process. As the number of variables affecting the conversion to energy increases, efficiency invariable decreases. Wood combustion is based on the most common exothermic process, in which carbon is oxidized to CO_2 by oxygen.

Wood consists of cellulosic material in which there are a wide range of oxygenated and hydrocarbon type organic compounds. Not surprisingly, alteration of the combustion conditions results in a myriad of byproducts including: carbon monoxide, particulate matter and a wide spectrum of organic species of which polycyclic aromatic hydrocarbon species (PAHs) are of greatest concern.

The factors that affect the combustion most are:

a) rate of oxygen supply - ventilation
b) rate of carbon supply - batch size, fuel composition, fuel type
c) temperature - stove characteristics, operating conditions

The other factor that affects the efficiency of combustion is temperature. These factors are further identified with respect to the characterization of emissions from residential woodstoves in the following paragraphs.

Fuel Characteristics

Aside from the numerous varieties of wood fuels, commercially produced newspaper logs, cardboard logs, compressed wood (with and without binders), treated wood, peat and bituminous coal are used to fuel stoves on the North American continent. The conditioning process of these fuels is a significant factor in determining the efficiency of the heating device and the emissions produced.

In Ontario, alternate fuels used to heat residences generally are limited to a few species of woods, and are listed below.

REGION	WOOD TYPES USED
Northwestern Ontario	Birch, jack pine, spruce
Central Ontario	Sugar maple, birch
Eastern Ontario	Birch

While newspaper logs and cardboard logs are used occasionally for ornamental fires in fireplaces, these fuels are extremely high in price and, hence, are not used for prolonged, nor intensive fuel combustion. For these reasons, discussion of fuels will be limited to commonly available wood types.

Soft and hard wood types generally have different heating values due to different composition, structure and density. Total particulate emissions by fuel type have been found to vary from 8.9 g/kg to 29 g/kg (Hartman and Rives, 1985). A typical emission rate for non-certified conventional woodstoves is around 20 g/kg (tested using Oregon/EPA Certification) (personal correspondence with J. Core). Fuel type effects also are dependent on burn-rate and, hence, in most studies, the variability caused by other effects within the same fuel type group has been overshadowed by factors such as stove type (Hartman and Rives 1985; Shelton and Gay, 1986). The study by Muhlbaier (1981) of emissions, from two softwoods and five hardwoods also confirmed this phenomenon. Typical particulate emission results (maintaining other variables of combustion as constant as possible) were:

- softwoods 11.9 ± 2 g/kg
- hardwoods 10.4 ± 2 g/kg

Surface Area

The log surface area is dependent on log size and geometry. Round logs with large diameter have the smallest surface area to mass ratio, in comparison with split logs and quartered logs. Emissions from residential wood combustion (RWC), therefore, also are influenced by log size and geometry. This effect has been explored by several researchers (Hubble et al., 1981; Cooke et al., 1982; Muhlbaier, 1981). Results indicated that particulate and organic emissions were considerably higher for the larger logs with smaller surface area to mass ratios (Muhlbaier, 1981).

However, CO emissions increased drastically with an increased surface area to mass ratio (Cooke and Allen, 1982) from 20 (lb/1000 lbs of wood) to 110 (lb/1000 lbs of wood) for surface area to mass ratios of 10 ft^2/ft^3 to 40 ft^2/ft^3, respectively.

Moisture Content

The moisture content of fuel wood has been known to influence the rate of combustion and the resultant emissions since man discovered fire. This factor of combustion has been studied extensively, and a good insight to the effects of moisture is presented in the following table (Weston, 1989). As evident in Table 1, particulate emissions increase significantly with increased moisture within the fuel wood. This effect is especially emphasized when values are normalized to the actual heat gained by the combustion process.

Operating Conditions

Operating conditions of the woodstove influence the combustion temperature and consequently the emissions generated. The study of the relationship between operating conditions and the resultant emissions is complicated by the stages of burning (burn cycle) (Hayden and Braaten, 1985), the stove type (Shelton and Gay, 1986), and the energy demand (heat required in relation to stove efficiency and rate of burning). The resultant physical factors produced by the above variables of combustion have been studied by numerous investigators and have been summarized in a concise diagram by Hubble et al., (1981) presented as Figure 1. The resultant emissions are highly dependent on these physical factors and these have been summarized for various stove types by Kowalczyk, Bosserman and Tombleson (1981).

Source Testing

The need for a standard source testing method was clearly recognized by the U.S. EPA and the standard EPA Methods 5G and 5H were developed for woodstove testing. While information exists for various airtight stoves, catalytic stoves, and the prototype wood pellet stoves, each stove type is unique in terms of characterization of emissions. Chemical characterizations of the RWC source generally have employed the specific test conditions of EPA modified Method V to identify the effect of factors such as wood type (e.g., oak or fir), and size of wood logs (6 inch diameter) with a common box type airtight stove (Rau, 1988).

Unfortunately, these test conditions do not reflect the actual conditions of RWC in Ontario. Firstly, the wood types used in the source characterization test performed to date are not in common use in Ontario. Oak is a comparatively expensive type of wood in Ontario and very little fir is grown because of local climate. Another variable that has not been addressed in the literature reviewed are emissions from Canadian manufactured woodstoves. Two very common types of woodstoves employed in Ontario are Kerr Titan and Fawcett WF 200.

Methods for source sampling of woodstoves for particulate emissions and organic compounds have been standardized (Cooke et al., 1984). The focus of the methodology is to quantify emissions from a specific stove type under rigorously defined conditions. The general methodology employs a standard type air-tight stove, with a sampling port that enables a sampling probe to collect a representative sample of the resultant mixture of flame gases and

TABLE 1

Impact of Moisture on Wood Net Heat Content and Particulate Emissions[1]

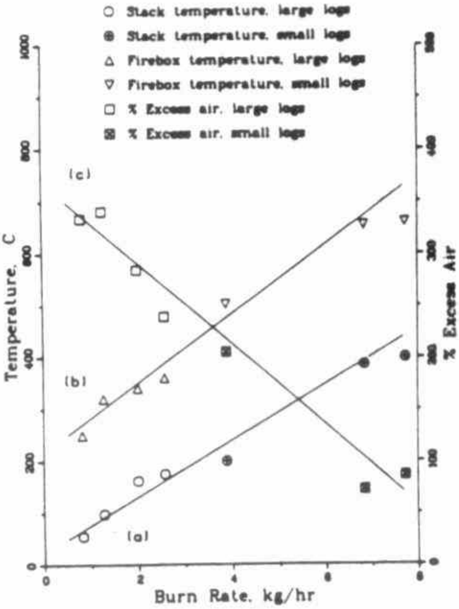
WOOD MOISTURE* CONTENT (%)	RELATIVE ENERGY CONTENT	RELATIVE PARTICULATE EMISSIONS PER POUND WOOD BURNED	RELATIVE PARTICULATE EMISSIONS PER NET BTU CONTENT OF WOOD BURNED
10%	1.00	1.0	1.00
20%	.88	1.2	1.36
30%	.67	1.5	2.25
40%	.59	1.9	3.22
50%	.47	2.4	5.10

* Wet basis, i.e., 10% moisture content = $\frac{\text{10 lb. water}}{\text{10 lb. water + 90 lb. wood}}$

[1] From Weston, 1989

FIGURE 1

Summary of Stack Temperature [curve (a)], Firebox temperature [curve (b)], and % Excess Air [curve (c)] versus Burn rate from Combustion of 0.12 -m- and 0.06 -m- Diameter Oak Logs.



suspended particulate matter (Allan et al., 1984). The following conditions have been standardized:

- wood species, size and shape (oak logs, 20 cm diameter);
- moisture content (20% W/W wet basis);
- minimum burn time;
- minimum sampling time;
- fuel charge weight (10 kg, dry);
- sample size (3 m^3 (STD, dry)); and
- steady-state operation.

While the purpose of standardizing these factors is to facilitate comparison between emissions from different stove types, these conditions do not reflect actual operating procedures and practices, local climate or local fuel wood types used.

The U.S. EPA emission factors discussed earlier are based on average values obtained through the standard testing procedure, conducted in various climatological locations. While these emission factors allow for an estimation of national emissions in the United States, their representativeness and applicability have been under review by the Inventory Management Division of Environment Canada. It was concluded that further work is required to quantify emission factors that reflect regional and temporal variability characteristics of Canadian Climates (Yandle, 1989) and wood fuels.

Residential Wood Combustion and Ambient Air Quality

A variety of objectives have motivated ambient air quality monitoring studies in areas with RWC impacts. One of the major objectives has been to determine the contribution of RWC emissions to ambient air quality - especially in regions with poor air quality (where existing ambient air quality standards are exceeded). Often, there are parallel studies for indoor monitoring to determine exposure of inhabitants while indoors, source characterization of emissions, as well as parallel surveys to determine wood consumption. Samples collected are analyzed for elemental species, ionic species, carbon analyses (C-14 isotopic composition, volatilizable (C_{vol}) and elemental carbon (C_{el})), a wide range of organic compounds - usually classified into polynuclear aromatic compounds (PAH), volatile organic compounds (VOC), as well as for the traditional pollutant gases (especially CO and NO_x). Recently, monitoring to determine the mutagenic activity of samples dominated by RWC emissions has been conducted.

Sampling Methods

Depending on the study objectives, sampling methods collect material for elemental (mainly inorganic), organic or biological data in three phases or modes:

1. particulate fraction;
2. gaseous fraction; and
3. combined particulate/gaseous fractions.

The sampling and to a lesser extent, analysis techniques that are used to determine ambient RWC impacts depend on the fraction required and hence, it is convenient to discuss methods for the collection of material in these phases.

Sampling of Particulate Phase Species

Sampling methods for ambient suspended particulate material commonly employ filter impaction of a known volume of air drawn through the filter matrix. Sampler types used include high volume samplers with or without size selection, and dichotomous samplers.

High volume samplers collect total suspended particulate matter, i.e., a full size range considered to contain particles of aerodynamic diameter 100 µm and less. Sampling rates are typically 1.13 to 1.70 m^3/min (40 to 60 ft^3/min). Samples generally are collected over a 24-hour period although some studies have used 12-hour (day/night sampling) sampling periods. Since particulate emissions from RWC appliances are predominantly in the 0.1 to 1.0 µm diameter size range (e.g., Kowalczyk and Greene, 1981), size selective sampling is often employed for ambient monitoring of RWC impacts. With the aid of a size selective inlet, high volume samplers collect suspended particles with a predetermined maximum cut-off diameter, typically 10 µm. When fitted with cascade impactors, high volume samplers collect particles in a number of particle diameter size ranges typically ~0.5 to 10 µm. Other samplers involving collection of particles on filter media, are in use and employ lower flow rates (low and medium volume samplers) with size selection of particles.

Dichotomous samplers have been the samplers that have been employed frequently in monitoring programs associated with the assessment of ambient RWC impacts. These samplers collect particles in two size ranges, usually < 2.5 µm (the fine or inhalable fraction) at (usually) 1.67 L/min, and 2.5 to 15 or 10 µm diameter - the coarse fraction at flow rates of (usually) 15 L/min. However, a limitation of low volume sampling is the possibility of filters plugging up in areas of heavy woodsmoke impact.

Sampling of Vapour Phase

The collection of vapour phase compounds is complicated by several factors:

- volatility;
- reactivity;
- break-through threshold; and
- stability of and consistency of sampling medium.

Gaseous compounds are not collected efficiently using filter paper impaction and adsorption; instead, actual volumes of air are collected, or alternatively, the vapour phase compounds are absorbed onto media that retain gaseous compounds with integrity over time. Sampling methods that have proven successful for gaseous compounds are:

- adsorbent tubes;
- tedlar bags;
- stainless steel canisters;
- direct cryogenic trapping; and
- impinger trains (generally used for source sampling).

Adsorbent tubes have been used extensively and the medium commonly used to adsorb low molecular weight hydrocarbons is activated charcoal. For a wider range of organic compounds, sorbent tubes are packed with tenax, carbosieve (molecular trap), fluorosil etc.; either exclusively or in combination. Since flow rate influences collection, and non-linearity and breakthrough occur in the high concentrations, the sampling protocol specifies up to four tubes be exposed in parallel. The quadruple sampling and analysis renders this method of sampling as costly, in comparison to Tedlar bags and canisters.

Combined Particulate and Gaseous Sampling

Several studies have been undertaken to determine the vapour particle distribution in Hi-Vol sampling (Cautreels and Van Cauwenberghe, 1977: Galasyn et al., 1984; Thrane and Mikalsen, 1981; Yamasaki et al., 1982; Davis et al., 1983; Dann et al., 1989) and also in low volume sampling (Bjorseth and Eklund, 1979; Andersen et al., 1988; Otson and Hung, 1983).

The distribution ratios of particulate to gas phase concentration of several PNA's as well as other classes of organics were reported by Cautreels and Van Cauwenberghe. For phenanthrene, anthracene, methylpyrene and methylanthracene, the distribution factors were 0.027 to 0.088; thus most of these compounds are in the gas phase. Fluoranthene, pyrene and benzofluorenes had intermediate values 0.26, 0.49 and 1.25 respectively while benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluranthene, benzo(a)pyrene, benzo(e)pyrene and perylene were primarily in the particle phase with distribution factors ranging from 3.14 to 11.5.

In some cases, more sensitive methods of analysis are desirable, such as neutron activation analysis (for elemental composition), and gas chromatography with mass spectroscopy (GC/MS), for organic and inorganic compounds.

Ambient concentrations are generally in the range of parts per billion (ppb) and thus, highly sensitive methods of analysis are required. Analytical methods commonly used to determine ambient concentrations include:

- gas chromatography (GC);
- gas chromatography with mass spectroscopy (GC/MS);
- ion chromatography (IC);
- high performance liquid chromatography with ultraviolet fluorescence (HPLC/UV-fluorescence);
- atomic absorption (AA);
- inductively coupled plasma (ICAP);
- thermal optical reflectance (TOR);
- neutron activation analysis; and
- X-ray fluorescence.

Studies to evaluate the impact of emissions from residential wood combustion initially examined the particulate emissions in the fine size fraction (0.01 to 1.0 μm) since source testing information indicated that most (> 90%) of the particulate emissions from RWC were in the fine fraction (Muhlbaier, 1982). Airshed studies focused on upwind/downwind mass loadings in the fine fraction. This was frequently accompanied by questionnaires addressing burning practices of the homes sampled. The need for better source resolution is evident, since all combustion sources display similar particle size distributions. Subsequent studies have followed the following designs:

a) upwind/downwind with particle sizing and chemical analysis;
b) outdoor sampling with source apportionment (using inorganic and organic woodsmoke characterizations); and
c) tracer studies.

Impact Studies in the United States

During the late 1970's and 1980's the rise in interest in RWC and the accompanying environmental concerns prompted air monitoring studies in several areas of suspected impact. Issues of non-attainment of aerosol and CO objectives prompted federal action to investigate the effects of residential wood combustion in various US EPA programs.

The major pre-1985 U.S. studies have been reviewed with respect to strategy and methodology employed in an EPA study (Hartman and Rives, 1985). Ambient data from the major RWC studies were compiled in a Technical Support Document (EPA-450/4-85-012). The ambient air quality data were summarized with references as part of this study. Average RWC impact determined in these studies were estimated for the fine mass fraction. The percentage contribution of RWC to the fine fraction ranged from 1.5% to 72.8%. Average ambient concentrations of carbon monoxide ranged between <1 ppm to 2.7 ppm (8 hour average). Of major concern in RWC studies, has been the incremental burden of benzo(a)pyrene (BaP) caused by woodsmoke emissions. Ambient BaP levels in one U.S. location was found to be above 100 ng/m^3.

The physical and chemical characteristics of emissions caused by most combustion processes are so similar that this grouping of sources is extremely difficult to separate. The overlapping nature of temporal and spatial distributions of sources, such as residential wood combustion and automotive emissions, also augment these difficulties.

An average source profile for residential woodstoves has been compiled by several investigators in the following locations: Medford, Oregon, Portland/Seattle and Pocatello, Idaho. These profiles have been provided by J. Core and are included in Figure 2, however, the aforementioned conditions and limitations restrict the usefulness and applicability of these profiles.

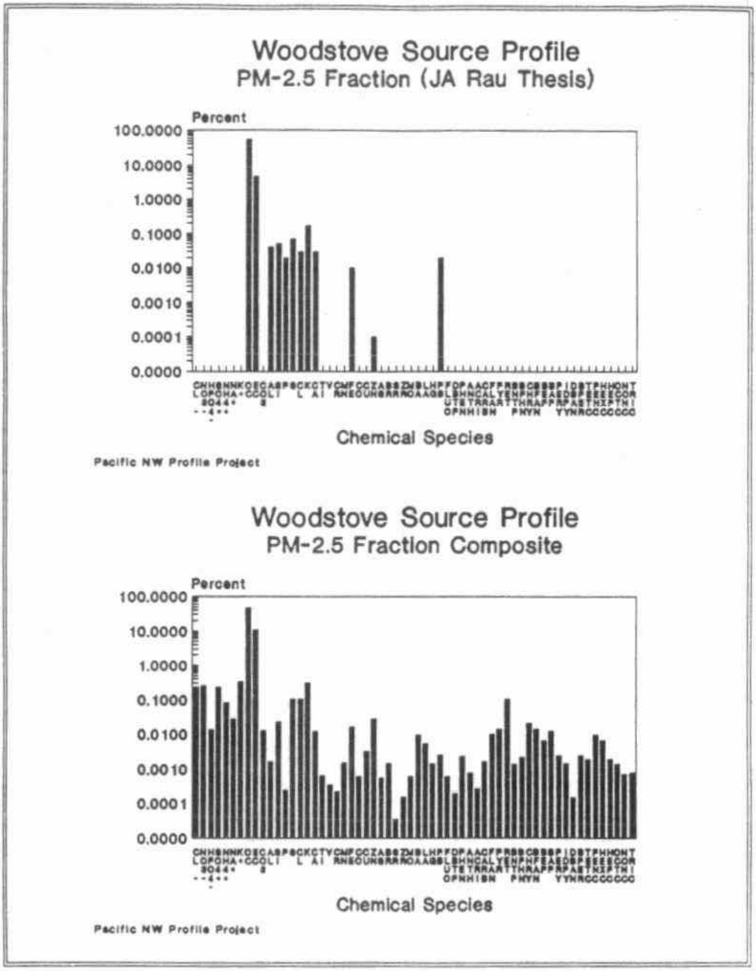
A variety of methods, and combinations of such, have been used to resolve woodsmoke emissions from other sources. The objective of assessing relative source contributions can be categorized into two domains:

i) statistical methods; and
ii) direct identification methods.

Statistical methods have evolved from hypothesis testing, multivariate regression techniques, factor analysis and matrix reductions. Mathematical models also have been developed to simulate indoor and outdoor dispersion of source emissions. Specifically, the methods of source apportionment that are statistical in nature comprise:

- hypothesis testing (e.g., upwind/downwind comparisons);
- regression techniques (least-squares, linear, curvilinear and multivariate);
- factor analysis (an extension of the multivariate regression techniques employing matrix manipulations);
- chemical (or elemental) mass balance (simultaneous solving of linear mass balance equations); and
- mathematical simulation equations (dispersion modelling).

FIGURE 2



Woodstove Source Profile
PM-2.5 Fraction (JA Rau Thesis)

Pacific NW Profile Project

Woodstove Source Profile
PM-2.5 Fraction Composite

Pacific NW Profile Project

Statistical methods have evolved from single variable regression to more sophisticated methods such as CMB analysis and mathematical simulation (modelling) for numerous environmental concerns. Whether the source is simple or complex; if the emissions from a process or reaction are easily identified with accuracy and reproducibility, these sources can be resolved with an average characterization of the source. The variabilities that impinge upon wood burning emissions characterizations, represent new challenges in source apportionment techniques. The direct methods of RWC emissions identification, probe for direct evidence of the source's influence on ambient samples. Two common methods of identification are:

- morphological investigation; and
- source tracing via tracer compound(s) or other source characteristic(s).

Conclusion

This review has cited studies of several areas in the U.S. and Canada in which there have been adverse air quality impacts. The climate of most areas is similar to that in Ontario - in the sense of winter temperatures; and for several areas that are located in mountainous areas and with orographic features (valleys, bowl shaped topography) conducive to poor dispersion conditions. However, the potential for adverse RWC air quality impacts are largely dependent on the extent of RWC use. In areas where there is heavy use of residential wood fuel, the potential will therefore exist. In order to assess the potential impacts, the obvious action is to conduct specific monitoring activities to assess the extent of the impacts. Methods for conducting such assessments, and factors that should be addressed in such a study have been reviewed. These factors specify the scope of the required study. In particular, the assessment could involve ambient air monitoring and analysis tracer methodology (e.g., potassium), and source characterization and data analysis, such as receptor modelling (Chemical Mass Balance (CMB)).

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A11

A STUDY OF THE PEAK OZONE LEVELS IN THE TORONTO AREA

By

J.D. Smith and L. Shenfeld
The MEP Company
Markham, Ontario

BACKGROUND

The concentration of ozone in the Toronto area exceeds Ontario's regulatory limit more often than any other pollutant. During the year Ontario's Air Quality Index was first introduced, (June 1988 to May 1989), Shenfeld and Yap (1989) reported that between 80 and 95% of the hours that the Air Quality Index was in the Moderate to Poor range within Metropolitan Toronto, ozone was the major pollutant. Furthermore, during the summer of 1988, the ozone hourly averages were frequently well above 120 ppb, (AQI=50), which is known to cause an impact on health to a large percentage of the population, especially those who may be exercizing outdoors. These high ozone developments occurred during periods of long-range transport (LRT) of ozone and precursors into the Province from United States. During the summer of 1989, the occurrences of high ozone readings were much less frequent, as the LRT conditions were not as prevalent, even during ozone conducive weather such as warm, sunny and relatively windless conditions.

Kurtz et al. (1989) have utilized the long-range transport Acid Deposition and Oxidant Model (A.D.O.M) to show the influence of U.S. emissions of nitrogen oxides and reactive hydrocarbons to the levels of ozone in Southern Ontario. Air mass back trajectory studies, most recently by Yap et al. (1988) established that U.S. sources of these pollutants were responsible for much of the high ozone values reported in Southern Ontario.

Ozone studies by Shenfeld (1977), Mukammel et al. (1982), and more recently Yap et al. (1988), established the meteorological conditions required for the development of high ozone levels in Southern Ontario. Studies of ozone developments in other geographical locations by Revlett (1978), Wolff and Lioy (1978), Prior et al. (1981), Simpson et al. (1983), and Robeson and Steyn (1990) have established that peak hourly average levels of ozone can be correlated to specific meteorological parameters.

STUDY OBJECTIVES

The main objective of this study is to determine the proportion of the peak ozone levels in Toronto resulting from the LRT of precursors and ozone into Toronto. A second objective is to determine whether the relationship between peak ozone levels and meteorological parameters can be used to predict the peak ozone levels and hence the Air Quality Index for the afternoon and early evening. The third objective is to determine the relationship between the peak hour ozone level and the maximum 8-hour average the same day and what the 8-hour averages are with peak hour levels of 80 ppb (moderate air quality) and 120 ppb (poor air quality).

STUDY DESCRIPTION

For this study, we have selected the peak hour ozone levels during each day from May to September inclusive, for the years 1988 and 1989, during which the Pearson International Airport reported temperatures equal to or exceeding 23°C and the cloud cover was equal or less than four tenths opacity. The selected days were then separated into days that LRT occurred from the industrial States and those that it did not. This classification was determined by using synoptic weather maps and the Ontario Ministry of the Environment Air Resources Branch archives of the back trajectories of air into Toronto.

Three Metropolitan Toronto ozone recording locations were selected for study, namely; Downtown Toronto (Breadalbane), Scarborough (Lawrence and Kennedy) and North York (Yonge and Finch).

For LRT and non-LRT days, multiple regression equations are used to relate the peak ozone levels at each of the above locations with the Pearson International Airport maximum temperature, average wind speed and average cloud cover during the hours of 9AM to 4PM. Another dependent variable used, is the peak hour ozone level measured the previous day at the rural station outside Simcoe, Ontario. The difference between the peak ozone levels determined from equations with LRT and with non-LRT is used to determine the contribution of ozone to the Metropolitan Toronto locations due to LRT.

REGRESSION ANALYSIS

A multiple regression analysis was completed for the three sites (Toronto, Scarborough and North York) for each of LRT and non-LRT days. A simple regression equation was derived from the ozone data set of the Ontario Ministry of the Environment:

$$Y = B_o + B_1 *X_1 + B_2 *X_2 + B_3 *X_3 + B_4 *X_4 \qquad (1)$$

where:
Y - Maximum Ozone Level (PPM)
X_1 - Maximum Temperature (°C)
X_2 - Average Wind Speed (Km/hr)
X_3 - Average Cloud Opacity (10^{ths})
X_4 - Previous Day's Maximum Ozone (PPM) Recorded at Simcoe, Ontario

The results of the regression analysis are outlined in Table 1.

The overall significance of the multiple regression can be tested by an analysis of variance. This test is equivalent to testing the null hypothesis that in the population from which the observations have been sampled, there is no significant regression of the dependent on the independent variables. The test consists of determining the F ratio for each case, that is the ratio of the mean square of the sum of squares of the regression over the mean square of the sum of squares of the residual. If the computed F exceeds the tabled value for a selected level of confidence, then the null hypothesis is rejected.

The F ratio is found at the bottom of Table 1. In all cases, the null hypothesis can be rejected at 5% level of confidence.

The effect of LRT from the industrial United States can be determined, at any particular site, from the difference in the predicted ozone levels using identical values for the independent variables in both the LRT and non-LRT regression equations. This difference was determined by using the above equations and all combinations of: air temperature being equal to 23, 27, 30 and 34 degrees C, wind equal to 0, 5, 10 and 20 km/hr., cloud cover equal to 0, 2, and 4 tenths, and the previous day's ozone equal to 40, 60, 80, 100 and 120 ppb. The results showed a minimum increase due to LRT to be 24.2% (13.7 ppb), a maximum increase of 48.7% (38.1 ppb) and an average of 31.7% (25.9 ppb). However, it can be expected that the effect of LRT to increase ozone concentrations would be even greater than indicated in this analysis which does not take into account the difference in means. The mean of the previous day's ozone is 15 ppb larger during LRT than non-LRT days (see Table 1) and all of the regression equations are positively correlated with the previous day's ozone.

TABLE 1 : MULTIPLE REGRESSION EQUATIONS
MAXIMUM OZONE LEVEL PREDICTION
(MAY 1988 to SEPTEMBER 1989)

	TORONTO [LRT]	TORONTO	SCARBOROUGH [LRT]	SCARBOROUGH	NORTH YORK [LRT]	NORTH YORK
N	35	41	36	42	30	35
B_0	-71.798	-54.829	-59.189	-23.973	-66.524	-27.924
B_1	5.166	3.931	4.985	3.333	5.335	3.381
B_2	-1.026	-0.894	-1.330	-1.088	-1.047	-0.949
B_3	-0.524	-1.625	-0.679	-2.525	-1.902	-1.413
B_4	0.152	0.115	0.125	0.099	0.109	0.051
R	0.805	0.679	0.698	0.653	0.685	0.696
R^2	0.648	0.461	0.487	0.427	0.470	0.485
SE	15.410	19.777	17.515	19.556	21.621	12.941
$\underline{Y}$	72.818	55.133	76.111	56.000	77.268	57.241
$\bar{X}_1$	29.230	26.380	29.229	26.350	29.461	26.938
$\bar{X}_2$	14.153	13.128	13.952	12.886	14.231	15.257
$\bar{X}_3$	1.923	1.895	1.880	1.862	2.177	1.801
$\bar{X}_4$	72.659	55.967	72.756	56.563	74.146	57.931
F	14.375*	6.279*	8.653*	6.088*	10.161*	6.622*

N - Number of Observations
B_0 - Multiple Regression Coefficient (intercept)
B_1 - Multiple Regression Coefficient (for X_1)
B_2 - Multiple Regression Coefficient (for X_2)
B_3 - Multiple Regression Coefficient (for X_3)
B_4 - Multiple Regression Coefficient (for X_4)
R - Correlation Coefficient
R^2 - R-Squared
SE - Standard Error of the Estimate (PPB)
$\underline{Y}$ - Mean Measured Ozone (PPB)
$\bar{X}_1$ - Mean Maximum Temperature (C)
$\bar{X}_2$ - Mean Average Wind Speed (Km/hr)
$\bar{X}_3$ - Mean Average Cloud Opacity
$\bar{X}_4$ - Mean Previous Day's
Measured Ozone at Simcoe (PPB)
F - F - Ratio

Significant at the 5% Level of Confidence

MODEL TEST

The multiple regression equation, as a predictor of peak level ozone, was tested by using independent data sets from May to September 1987 for the Toronto and Scarborough sites. Measured peak ozone levels were compared against predicted peak ozone levels by using the appropriate regression equation, the relevant meteorology and the measured previous day's ozone at Simcoe. Figure 1 shows the graph of the total measured versus. predicted ozone levels for all study locations.

Willmott (1982), citing several examples showing that real significance and statistical significance do not exhibit a close correspondence, has proposed measures of 'systematic' and 'unsystematic' error to examine the types of differences and an 'index of agreement' to investigate the relative size of differences. Because a model should explain most of the major trends present in the observed record, it is important to know what proportion of RMSE is systematic ($RMSE_s$) and what proportion is unsystematic ($RMSE_u$). In this fashion, with respect to a 'good' model, $(RMSE_s)^2$ should approach zero while $(RMSE_u)^2$ should approach RMSE. The 'index of agreement' (D) was proposed to yield a measure of the relative size of differences; this index is intended to be a descriptive measure which is both relative and bounded ($0 \leq D \leq 1$) and can be widely applied in order to make cross-comparisons between models. As the agreement between the observed and predicted variables increases, D approaches 1.0 .

Table 2 contains the model performance statistics. It should first be noted that the calculated and measured population means and standard deviations are very similar, in fact in no case is the difference between the two means greater than 2 ppb.

The MAE and RMSE indicate a mean difference between the predicated and observed values of approximately 13 ppb. With the unsystematic portion of the RMSE being around 10 ppb, this indicates that most of the RMSE is unsystematic and it need not be assumed that there is a missing independent variable in the regression analysis.

The last column of Table 2 contains the model performance statistics for the combined "computed versus. measured" matrix. This is included to increase the size of the population to be 'large' (N>30) since the general utility of such indices as RMSE is questionable as N becomes small (Willmott, 1982). The high value of the Willmott Index of Agreement (D) (0.853) indicates a reasonably good agreement between the predicted and measured peak ozone levels.

FIGURE 1 : OBSERVED VS PREDICTED MAXIMUM OZONE LEVELS

TOTAL FOR 1987

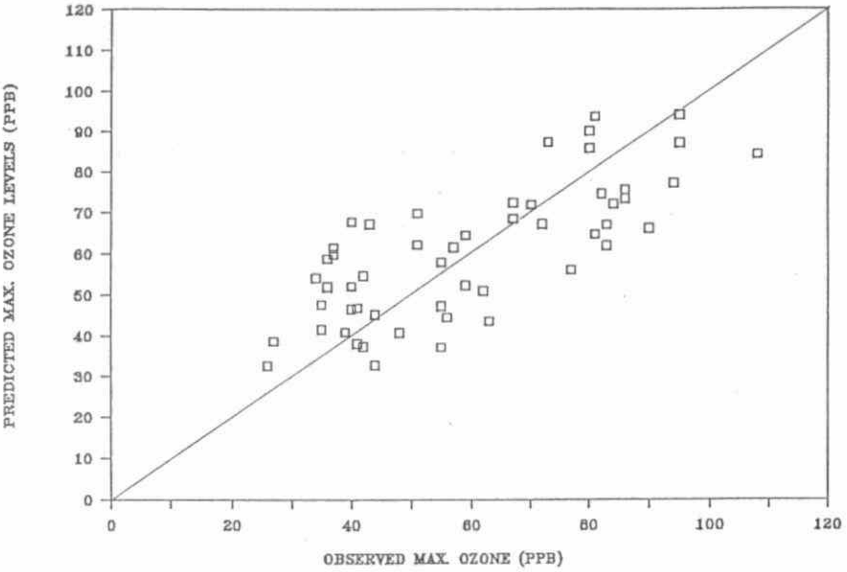

TABLE 2 : OZONE LEVEL PREDICTION
MODEL PERFORMANCE STATISTICS

	TORONTO [LRT]	TORONTO	SCARBOROUGH [LRT]	SCARBOROUGH	TOTAL	
N	12	16	11	15	54	- Number of Observations
O	69.000	48.312	73.273	55.866	60.092	- Average Observed Ozone
P	69.112	50.291	74.004	56.517	61.033	- Average Predicted Ozone
So	19.821	17.647	22.865	17.410	21.198	- Observed Standard Deviation
Sp	17.102	13.424	16.714	10.907	16.915	- Predicted Standard Deviation
a	0.603	0.528	0.470	0.422	0.604	- Slope of Regression Line (OBS vs PRED)
b	27.512	24.757	39.547	32.953	24.755	- Intercept of Regression Line
MBE	0.112	1.978	0.731	0.650	0.940	- Mean Bias Error
MAE	11.872	10.557	15.256	10.556	11.806	- Mean Absolute Error
RMSE	13.928	12.498	16.816	12.479	13.794	- Root Mean Square Error
RMSEs	7.537	8.295	11.572	9.747	8.376	- Systematic Portion of RMSE
RMSEu	11.713	9.348	12.201	7.791	10.959	- Unsystematic Portion of RMSE
R^2	0.488	0.483	0.413	0.453	0.573	- R-Squared
D	0.821	0.816	0.764	0.763	0.853	- Wilmott Index of Agreement

8-HOUR AVERAGE OZONE LEVELS

The final part of this study deals with the relationship between the peak hourly ozone level and the 8-hour average on the same day. The data set used for the determination of the regression equations is used here to determine the linear regression between the observed peak ozone (Y) and the 8-hour average (X_o) by the equation:

$$Y = B_o + B_1 * X_1 \qquad (2)$$

Table 3 shows the linear regression equation for each site and for each of LRT and non-LRT days. From the table we can see a high level of correlation with an average correlation coefficient (R) of 0.95 and an average coefficient of determination (R^2) of 0.89 . Using these linear equations it is possible to estimate the 8-hour average associated with a peak hourly ozone level of 80 ppb (moderate air quality) and 120 ppb (poor air quality). These values are listed on Table 3 and are equal to, on average, 62 and 91 ppb, respectively. Figure 2 shows graphically the total relationship between peak hourly ozone and the 8-hour average ozone for all study locations.

SUMMARY AND CONCLUSIONS

This study has determined that the level of ozone in Metropolitan Toronto increases on LRT days. These increases in ozone averaged approximately 32% (26 ppb) and peaks as high as 49% (38 ppb) were noted. These results are compared with Wolff and Lioy (1978), who concluded by a similar means that the contribution of external sources to a Connecticut location during high ozone days, was as much as 75 ppb, and Prior et al. (1981) reported the LRT contribution to St. Louis was 36 ppb.

Multiple regression equations were determined relating the peak hour ozone levels with the same day maximum temperature, the average daytime windspeed and the cloud opacity at Pearson International Airport and the peak hour ozone concentration at the Simcoe rural station for the previous day, for LRT and non-LRT days in 1988 and 1989. Data for 1987 were used to validate the statistically determined relationships. These equations have proven to be reasonabley good predictors of peak ozone levels in the Metropolitan Toronto area.

FIGURE 2 : 8 HOUR AVERAGE VS PEAK HOURLY OZONE
TOTAL FOR 1988-89

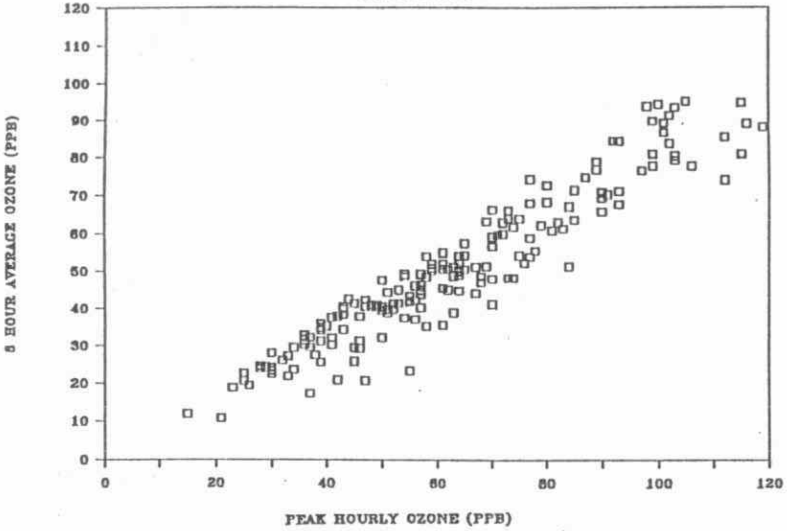

TABLE 3 : LINEAR REGRESSION EQUATIONS
8 HOUR AVERAGE OZONE LEVEL PREDICTION
(MAY 1988 to SEPTEMBER 1989)

	TORONTO [LRT]	TORONTO	SCARBOROUGH [LRT]	SCARBOROUGH	NORTH YORK [LRT]	NORTH YORK	
N	35	41	36	42	30	35	- Number of Observations
Bo	0.495	10.177	1.886	4.479	-4.196	5.210	- Linear Regression Coefficient (intercept)
B1	0.772	0.631	0.766	0.682	0.855	0.714	- linear Regression Coefficient (for X1)
R	0.985	0.943	0.943	0.964	0.945	0.948	- Correlation Coefficient
R^2	0.918	0.889	0.889	0.930	0.893	0.899	- R-Squared
SE	5.993	5.430	6.296	5.220	8.512	5.244	- Standard Error of the Estimate (PPB)
Y	56.152	41.379	59.494	41.941	62.383	45.610	- Mean 8 Hour Average Ozone (PPB)
X1	72.818	55.133	76.111	56.000	77.268	57.241	- Mean Peak Hourly Ozone (C)
MOD. LEVEL	62.225	60.657	63.166	59.039	64.204	62.330	- Value of 8 Hour Average Calculated for a Peak Ozone Level of 80 PPB
POOR LEVEL	93.135	85.897	93.806	86.319	98.404	90.810	- Value of 8 Hour Average Calculated for a Peak Ozone Level of 120 PPB

The study also indicated that Ontario's 80 ppb one-hour average regulatory limit cannot be used as a surrogate for an eight-hour average health standard. The World Health Organization Guidelines recommend 50 to 60 ppb for an eight-hour average level of ozone for the protection of human health.

Similar studies could be carried out in the future to determine regression equations for peak hourly ozone for other cities of Southern Ontario, for both LRT and non-LRT days. The regression equations can be used to predict the peak ozone levels and the associated AQI for each location.

ACKNOWLEDGEMENTS

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A12

DEVELOPMENTS OF MONITORING METHODS FOR ODOROUS ORGANICS IN AMBIENT AIR

C.C. Chan, P. Forsythe, L. Vainer, J.W. Martin
Mann Testing Laboratories Ltd.
5550 McAdam Road
Mississauga, Ontario, Canada
L4Z 1P1;

INTRODUCTION

Odour nuisances have been reported in connection with facilities such as water treatment plants, kraft mills, rendering plants and oil refineries. The problem is that often the odour detection limit for the airborne compounds are lower than the current analytical detection limits: this is true particularly with sulfur containing compounds.

In the present study we have evaluated recent methods for the detection of four classes of compounds associated with odour complaints: aliphate amines; carbonyl compounds; short chain fatty acids; and sulfur containing compounds. With the exception of certain target sulfur compounds (for which we use thermal desorption/GC/MS)[1], the process of chemical derivatization followed by HPLC using either U.V. or fluorescent detection appears to be the best approach for obtaining detection limits in the low parts per billion range for most compounds under study.

METHODS

I AMINE ANALYSIS

SAMPLE PREPARATION[2]

Sep-PAK C_{18} cartridges were purchased from Waters Scientific, Mississauga and prepared as described below.

The Sep-PAK is initially washed with 5 mL methanol by attaching a syringe full of the solvent to the luer-look end of the cartridge and slowly passing methanol through. A second wash is then performed with a 3% (V/V) phosphoric acid solution in methanol using the same technique as above. The two ends of the Sep-PAK are then touched to a kimwipe, in order to remove any excess liquids.

The Sep-PAK is then placed in a vacuum manifold (Supelco Canada Inc.) and dried for one hour under reduced pressure and a nitrogen stream. Following this, the cartridge is placed directly under a stream of nitrogen for one half hour and a flow-rate of 80-100 mL/minute. The Sep-PAKS are placed in individually capped and labelled glass vials, and stored in a cool, dark, dry place for up to four weeks.

SAMPLING

Ambient air is drawn through the Sep-Pak cartridge at a known rate. The rate of pumping is measured before and after sampling

ANALYTICAL PROCESSING AND DERIVATIZATION

A stock basic methanol solution is prepared by weighing 0.166 g of KOH (BDH, Toronto) and dissolving it in 100 mL of distilled-in-glass methanol (Caledon, Georgetown). The derivatizing solution is made up by dissolving 0.200 g of 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl)(Aldrich) in 100 mL of the above basic methanol solution.

A 1 mL aliquot of NBD-Cl solution is then pipetted into 10 mL capped and labelled centrifuge tubes. Into these tubes the trapped amines are eluted by passing 5 mL of potassium hydroxide/methanol stock solution through the Sep-PAK cartridge. The tube is capped, vortexed for several seconds and incubated for a minimum of 24 hours at room temperature.

ANALYTICAL SYSTEM AND CONDITIONS

A Hewlett Packard model HP1090 HPLC system with the following components is used:

- gradient solvent delivery system
- variable volume injection system with autosampler
- variable wavelength, programmable fluorescence detector
- integrator with a data system
- heated column compartment

The column necessary for the separation of the amines is Supelco's Supelcosil LC-18-S, a base deactivated, reversed phase octadecylsilane column. The column dimensions are: 25 cm x 46 mm with a 5 um particle size. The chromatographic conditions are listed below.

SOLVENT DELIVERY

Initial:	45% methanol, 55% water
6 minutes:	60% methanol, 40% water
Run time:	15 minutes
Flow rate:	1.5 mL/minute
Column Oven Temp:	40°C
Injection Volume:	20 uL

DETECTION

Lambda Excitation:	470 nm
Lambda Emission:	530 nm
Photomultiplier Tube Gain:	18 (maximum)
Response Time:	1000 msec

II **ALDEHYDES AND KETONES ANALYSIS:**

DNPH SOLUTION FOR COATING SEP-PAKS[3]

20.0 ml of saturated DNPH solution are added to 200 ml acetonitrile in a 1L volumetric flask with glass stopper. 1.0 ml conc H_3PO_4 is added, and solution shaken and made up to 1L volume with acetonitrile. The purity level of the solution is checked using HPLC.

COATING OF SEP-PAK CARTRIDGES

Each Sep-Pak is flushed with 10.0 ml acetonitrile using 10-ml syringe. An 7.0 ml aliquot of DNPH solution is dispensed through the Sep-Pak at a rate of 2.0 ml/min.

U.H.P. grade nitrogen is blown through the Sep-Paks via a DNPH guard column and drying manifold. (The use of paper towels should be avoided as these contain formaldehyde), at the rate of 50-100 ml/min for a few minutes (until no excess solvent droplets appear. Cartridges are then plugged at each end with luer lock male plugs and stored individually in glass culture tubes with either Teflon or polypropylene caps (Bakelite caps should be avoided as they are a source of formaldehyde)

PREPARATION OF DNPH-CARBONYL STANDARDS[4]

FORMALDEHYDE, ACETALDEHYDE, PROPIONALDEHYDE, ACETONE

A saturated solution of DNPH in 2N HCl is titrated with each of the above carbonyl compounds. The colored precipitate is washed with 2N HCl and water and air dried. Purity of derivative is determined by HPLC.

ACROLEIN, BUTYRALDEHYDE, BENZALDEHYDE, GLUTYRALDEHYDE[5], CYCLOHEXANONE (INT. STD).

The DNPH derivatives of these compounds are prepared by adding the carbonyl compound dropwise to an acidic solution of DNPH in dimethylsulfoxide (DMSO). The colored precipitate is filtered and washed with 2N HCl, and water. Purity is checked by HPLC. Individual stock solutions are prepared by dissolving 10 mg. of solid derivative in 100 ml of acetonitrile. A stock mixture of derivatives is similarly prepared.

ANALYTICAL PROCESSING

Sep-Paks are eluted with 3.0 ml acetonitrile using a 5.0 ml syringe giving a final volume of 2.8 ml of eluent.

Samples are run on Hewlett Packard HPLC 1090A system using the following equipment and conditions (Figure 2).

Phenomenex 150 mm x 4.6 mm. ODS C_{18} column (or equivalent).

Hewlett Packard Diode array detector (or equivalent)

Solvent: 60% acetonitrile, 40% water.
Flow 1.0 ml/minute
Analytical wavelength 360 nm.
Oven temp. 40°C

GLUTYRALDEHYDE (1,5-PENTANEDIAL)

The following analytical conditions are used to chromatograph the DNPH derivative of glutyraldehyde.

Column: Zorbax CN column 4.6mm x 150mm
Mobile Phase
55% acetonitrile / 45% H_2O / 0.1% H_3PO_4

III CARBOXYLIC ACID ANALYSIS

PREPARATION OF STANDARDS[6]

1-Pyrenyl diazomethane (PDAM). 50 mg of 1-pyrenecarboxaldehyde is suspended in 3 ml DMSO ; 0.3 ml of hydrazine monohydrate is added with stirring, and the mixture stirred at 50-60°C for 3 hours. The yellow crytals of 1-pyrenecarboxaldehyde hydrazone are filtered and recrystallized from ethanol. Purity is checked by HPLC.

To 20 mg of the hydrazone suspended in 5 ml of diethyl ether and added 65 mg of activated manganese dioxide and the resulting mixture allowed to react in an ultrasonic water bath for 90 minutes. The manganese dioxide is filtered and the reddish-orange filtrate evaporated to dryness under nitrogen yielding red crystalline PDAM.

DERIVATIZATION OF FATTY ACIDS

To 2 mg of acid in 2.0 ml methanol are added 2.0 ml of 0.4% w/v solution of PDAM in ethyl acetate. The mixture is stirred for 2 hours at room temperature after which time a single peak is obtained on the chromatogram.

SEP-PAK PREPARATION

C18 cartridges are loaded with 1% sodium hydroxide in methanol. The cartridges are dried by flushing with pure nitrogen.

Recovery studies using standard fatty acids loaded onto prepared Sep-Paks, elution, and subsequent derivatization indicate recoveries >80%.

ANALYTICAL PROCESSING

HP1090 system with fluorescent detection (lamda $_{ex}$ 340nm, lamda $_{em}$ 397nm)

Column: 15 cm Merck lichrosphere ODS (5u)
Solvent: 70% acetonitrile/30% water

STANDARD GAS GENERATION

Gas standards for individual target compounds are generated using a VICI Metronics dynacalibrator system, equipped with internal pump. Generated gas standards are diluted with zero air to give final concentrations in the low ppb range.

QA/QC

For samples a 20% QA/QC program should be implemented. This calls for 10% duplicate samples, 5% blanks and 5% spike recoveries.

RESULTS AND DISCUSSION

CHROMATOGRAPHY OF DERIVATIZED AMINES, CARBONYLS AND CARBOXYLIC ACIDS

Recoveries at three levels for target amines and carbonyl compounds are generally better than 85%. Preliminary studies on the carboxylic acids indicate similar recoveries.

Detection limits for target amine and carbonyl compounds are given in Tables 1 and 2. These detection limits correspond to a signal to noise ratio 5:1 and are determined by sequential dilution of stock standards. The ppbv values are based on an air sample of 150 litres for amines, and 100 litres for carbonyls.

CARBOXYLIC ACIDS AND SULFUR COMPOUNDS

Detection limits for target carboxylic acids are given in Table 3. It is clear that the derivatization of carboxylic acids using the fluorescent tag pyrenyl diazomethane (PDAM) provides a sensitive means of determining this class of compounds.

With the exception of butyric and isobutyric acid, which co-elute, good chromatographic separation is obtained for the remaining target compounds and recoveries from the C18 Sep-Pak are good (>80%).

The group of sulfur compounds owing to their reactivity, instability and low odour thresholds pose the greatest challenge. The thiols are amenable to derivatization using 7-Chloro-2, 1,3--benzoxadiazole-4-sulfonate (SBD-Cl) [7] with subsequent HPLC determination using fluorescent detection. Recent studies indicate that a structurally similar fluorescent tag may be used to derivatize disulfides[7,8]. We are presently investigating this in conjunction with a thermal desorption GC/MS method.

CONCLUSIONS

With the possible exception of sulfur compounds (methods for which are currently being evaluated) the process of concentrating airborne odorous compounds on to a suitable matrix, with either in-situ or post elution derivatization followed by HPLC, allows detection limits in the low ppbv range to be attained. Whilst the procedures are not new, the optimisation of variables (such as cartridge packing material, flow rates through the cartridge, pH of eluting solvent) combined with the development of a sampling train for field us for all four compound classes will provide the unique capability of narrowing the source of an odour problem to a compound group with subsequent quantitation.

TABLE 1

Method Detection Limits for the Analysis of Aliphatic Amines in Air

	Method Detection Limit (ppb)	RDS (%)	Degree of Error "D" (ppb)	Lower Limit (ppb)	Upper Limit (ppb)
Methylamine	0.105	6.36	0.011	0.093	0.117
Dimethylamine	0.043	4.99	0.001	0.041	0.044
Ethylamine	0.063	10.5	0.006	0.056	0.069
n-Propylamine	0.039	15.3	0.005	0.034	0.045
Diethylamine	0.809	13.6	0.129	0.68	0.938
n-Butylamine	0.040	5.1	0.001	0.039	0.042

TABLE 2

Method Detection Limits for Carbonyl Compounds

	Detn Limit ng for 20 ul inj.	*Detn Limit ppb_v	RSD %	Degree of Error "D"	Lower Limit ppb_v	Upper Limi t ppb_v
Formaldehyde	1.00	0.14	10.71	0.014	0.13	0.15
Acetaldehyde	0.90	0.13	18.45	0.022	0.11	0.15
Propionaldehyde	1.98	0.20	13.20	0.026	0.17	0.23
Butyraldehyde	2.30	0.25	24.80	0.058	0.19	0.31
Benzaldehyde	3.20	0.39	7.63	0.028	0.36	0.42
Glutyraldehyde	2.00	0.15	17.30	0.025	0.13	0.18
Acrolein	3.50	0.30	12.00	0.034	0.27	0.33
Acetone	3.00	0.25	16.40	0.039	0.21	0.29

* Based on a 100 litre air volume.

TABLE 3

Method Detection Limits for Fatty Acids*

	Detection Limit Femtomoles for 20 ul inj.	Detection Limit (ppt_v)	RSD (%)
Acetic Acid	100	6.0	12.5
Propionic Acid	200	12.0	13.9
Isobutyric/	300	18.0	14.6
Butyric Acid	200	12.0	10.8
Isovaleric Acid			
Valeric Acid	200	12.0	15.1

* Signal to noise ratio 5:1
ppt_v based on 100 litre air volume

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ATMOSPHERIC MEASUREMENTS OF NATURAL HYDROCARBONS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

H. Niki and B. H. Khouw

Chemistry Department
and
Centre for Atmospheric Chemistry
York University

BACKGROUND

This OME-sponsored project was initiated in 1988, as part of the Eulerian Model Evaluation Field Study (EMEFS), to obtain data on atmospheric concentrations of a number of key volatile organic compounds (VOC), particularly biogenic hydrocarbons such as isoprene and mono-terpenes. These data are needed for an assessment of the relative importance of NO_x and VOCs, and natural vs. anthropogenic VOCs in the oxidant and acid rain problems. Notably, international, national and provincial decisions on control strategies for oxidant precursors are at present in various stages of formulation. For example, the Federal/Provincial LRTRAP (Long Range Transport of Air Pollutants) Committee is developing a management plan for dealing with Canada's O_3 problem and meeting Canada's international obligations under the NO_x/VOC protocol [1]. There remain numerous outstanding scientific issues concerning the formation of O_3 and other oxidants. To review ongoing oxidant-related research in Canada and to identify the knowledge gaps to be addressed in the future, an National Oxidant Research Workshop was held recently under the auspices of CIRAC (Canadian Institute for Research in Atmospheric Chemistry) [2]. It was concluded at that workshop that there exists a critical lack of data on the temporal and spatial distributions of natural VOCs as well as their sources and emission rates in representative Canadian settings.

Scope of this project encompasses (1) the development of GC and GC/MS-based analysis of ambient C_2-C_{10} hydrocarbons; (2) measurements of these hydrocarbons at the Ministry's site at Dorset and other forested areas; and (3) statistical analysis and chemical modeling of the data thus obtained, in collaboration with other CIRAC scientists. While substantial progress is being made on all these research areas, this report will focus on the results of the analysis of the 1988 Summer EMEFS data to illustrate the current knowledge on the relative importance of natural and anthropogenic hydrocarbons in oxidant formation in Eastern North American rural atmospheres and on the meteorological factors controlling the atmospheric concentrations of isoprene, the dominant natural VOC emitted by deciduous trees. This Canada-US joint study represents the most extensive measurements of nonmethane hydrocarbons (NMHCs) carried out to date on a regional scale during summer months when multi-day O_3 episodes occur frequently. The PI has been requested by the participants to carry out site-to-site comparisons of these data to discern site-specific and regional features. Presented in this paper is a brief summary of these data analyses.

(I) 1988 Summer EMEFS Data on Hydrocarbons

Comprehensive measurements of speciated NMHCs were made concurrently during July and August in 1988 at four rural sites in eastern North America (i.e. Brasstown Bald, Georgia;

Dorset and Egbert, Ontario; and Scotia, Pennsylvania). These NMHC measurements were carried out together with other key atmospheric species as part of the enhanced ground site measurements of the EMEFS (Eulerian Model Evaluation Field Study) program [3]. The participants in the NMHC measurement program were groups from Georgia Tech. (Brasstown Bald); NOAA and U. of Washington (Scotia); and AES, OME, C & P, Hydro, Concord Scientific and York U. (Canadian sites). The data from Dorset and Egbert have been archived in an AES report [4].

A summary of the NMHC data obtained at the four rural sites are presented in Table 1. The NMHC compounds listed in these tables are representative of both natural and anthropogenic species but do not include all the identified species containing up to C_{10}. Namely, by class, the C_2-C_{10} hydrocarbons listed are: (1) alkyne and alkene (acetylene, ethylene and propylene); (2) alkane (ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, 2-methyl pentane, 3-methyl pentane, n-hexane, n-heptane and n-octane); (3) aromatic (benzene, toluene, o-, p- and m-xylenes and ethylbenzene); and natural NMHCs (isoprene, α- and β-pinene). α- and β-pinene were not measured by the Canadian group. The median concentrations indicated in this table are based on the data obtained between 8:00 to 17:00 EST. Night-time data were not included in these analyses because they are susceptible to influence of nocturnal inversion layer and also because natural NMHC isoprene emission presumably occurs only during the daytime [5]. The spread of the data is also shown in this table in terms of the data ranges of ±67 %. Inspection of the frequency distributions indicated that all the NMHC data are significantly skewed. Therefore, for the purpose of making site-to-site comparisons of these data, median values are judged to be more meaningful than mean values, and thus are used throughout the discussions presented below. For ease of visual inspection, concentrations of individual NMHC species at the four rural sites are shown graphically in Figures 1-4, for the four NMHC groups described above, i.e. alkyne and alkene, alkane, aromatic and natural compounds. Notable features of these site-to-site comparisons are annotated below.

Alkyne and Alkene (Fig.1): The data range for each of these hydrocarbons overlaps to a great extent from site to site. However, the median values plotted in this figure do exhibit an apparent trend of being lower at Brasstown Bald and Scotia than at either Egbert or Dorset. Acetylene concentrations are nearly identical at all sites, ranging from 0.58 (Brasstown Bald) to 0.83 (Egbert) in ppbC units. The ethylene concentrations at Brasstown Bald (0.30 ppbC) and Scotia (0.50 ppbC) are substantially lower than those at the other three sites, (0.70-0.93 ppbC). Propene concentrations exhibit greater site-to-site variability, as much as a factor of four from the lowest value (0.05 ppbC) at Scotia to the highest (0.21 ppbC) at Egbert. Greater temporal and spatial variability is to be expected for ethylene and propylene which are more reactive than acetylene toward HO radical by a factor of ≥ 10 [6].

Alkane (Fig. 2): Several features can be noted in this figure; (1) For the light alkanes from ethane up to n-pentane both absolute concentrations and relative distributions at all sites are very similar, within a factor of two; (2) Values for i-pentane measured at three sites are also seen to be nearly identical; (3) For the heavy alkanes from 2-methyl pentane to n-octane, the median concentrations are much higher, by a factor of three to ten, at Dorset and Egbert than at Brasstown Bald and Scotia, Scotia values being generally the lowest; and (4) both the absolute concentrations and relative abundances of these heavier alkanes are nearly identical at Dorset and Egbert. These observations (1)-(4) may be due in part to the degree of aging of urban air masses transported to these rural sites, the heavier alkanes being generally more photochemically reactive than the lighter alkanes [7].

Aromatic (Fig.3): In general, while the relative abundances of benzene, xylenes and ethylbenzene are similar at all sites, the absolute concentrations of these light aromatic compounds vary significantly from site to site (by a factor of up to 4 for benzene and a factor of ^10 for p- and m-xylenes), the highest values being consistently at Egbert and the lowest at

Scotia. The Scotia data also reveal significantly lower concentrations of xylenes relative to those of benzene and toluene than at the other sites, which may reflect photochemical aging of air masses transported to these sites. For instance, the HO-radical reactivity of xylenes is more than 10 times greater than that of benzene. However, interpretation of these site-to-site variations of median NMHC concentrations clearly requires more detailed information on air mass history for each site. Also, as to be noted in Tables 1-4, the data-set sizes for the aromatics are generally much smaller than those for alkanes at a given site and vary significantly from site-to-site, the largest (≥175 points per compound) being at Scotia and the smallest (≥23 points for o-xylene) at Dorset. Although no bias is apparent toward episodic conditions for data from both Dorset and Egbert, their small sample sizes make statistical comparison with the Scotia data less meaningful.

Natural NMHC (Table 2): The site-to-site variations of natural NMHCs are very large. Namely, median values of isoprene concentrations vary by over a factor of thirty in the ascending order of Egbert (0.84 ppbC), Dorset (3.59 ppbC), Brasstown Bald (12.2 ppbC) and Scotia (25.70 ppbC). Also, isoprene concentrations are shown in this table to be by far the highest in ppbC units among all the natural and anthropogenic NMHC species observed at all four sites, particularly at Brasstown Bald and Scotia. Median concentrations of α- and β-terpene on a carbon basis are approximately 10% of isoprene at Brasstown Bald and less than 1% of isoprene at Scotia. As will be discussed in later, these site-to-site variations in natural NMHC concentrations appear to reflect mainly the differences in the type and the extent of coverage of vegetation at each site as well as the temperature dependence of isoprene emissions from deciduous trees. Among the four measurement sites Egbert is the only site with few deciduous trees in the immediate vicinity, and is therefore expected to be the lowest in isoprene concentrations, in agreement with the observation.

(II) Atmospheric Oxidation Rates of NMHCs

For an assessment of relative importance of individual NMHC species in the formation of oxidants, particularly O_3, their atmospheric oxidation rates, (i.e. removal rates by atmospheric reactants) can provide a more meaningful measure than their actual concentrations. It is well-established that the atmospheric gas-phase oxidation reactions of alkane and aromatic hydrocarbons are initiated mainly by HO radicals, while the olefinic hydrocarbons such as propylene, isoprene and mono-terpenes can be oxidized significantly by both HO radicals and O_3. Rate constants for these relevant reactions are reasonably well known for the ambient temperatures encountered at these ground monitoring sites during the 1988 EMEFS program [7,8]. Thus, rates of reactions consuming the individual hydrocarbons can be calculated from the concentrations of speciated NMHCs observed at various sites (cf. Table 1), in combination with plausible experimental or theoretical values of the ambient concentrations of HO radicals and O_3, which were taken to be 5×10^6 molecule/cm^3 and 100 ppb (i.e. 2.5×10^{12} molecule/cm^3), respectively. These assumed values of HO and O_3 concentrations roughly correspond to those common to highly photochemically active daytime conditions at these rural sites [9,10]. Rates of oxidation thus calculated are plotted in Figure 4 for the twelve most dominant NHMCs. It can be readily noted that isoprene exhibits by far the largest oxidation rate among all NMHC species at all four sites. Also, α- and β-pinene are seen to be the next largest contributors to the overall NMHC oxidation rate at Brasstown Bald and Scotia. Thus, on the average, the natural NMHCs are the main hydrocarbon species responsible for controlling the local atmospheric chemistry at all four site.

For various anthropogenic NMHC types (i.e. alkene, alkane and aromatic), there are observable site-to-site variations in the relative rank of their oxidation rates. Namely, at Scotia the descending order of relative oxidation rates (n-butane = 1.00) is propylene(1.89), n-butane(1.00); i-pentane(0.92), ethylene(0.84), toluene(0.58), propane(0.46), i-butane(0.43), n-pentane(0.43), o-xylene(0.32), and m-, p-xylene(0.32). Thus, the alkene and light alkane compounds exhibit greater atmospheric reactivity than the aromatics at this site. On the other hand, the reactivity ranking at Brasstown Bald is somewhat reversed, the highest being the aromatic compounds, i.e. p-, m-xylene(2.61), toluene(1.70), o-xylene(1.19), n-butane(1.00), propylene(0.70), propane(0.61), n-pentane(0.60), ethylene(0.53), i-butane(0.35) and 2-methyl pentane(0.33). The reactivity trends for the Dorset and Egbert sites are similar to that of Brasstown Bald, but are more pronounced e.g. for Egbert p-, m-xylene(4.26), toluene(1.18), o-xylene(1.39), 2-methyl pentane(1.32), propylene(1.13), ethylene(1.06), i-pentane(1.03), n-butane(1.00), n-heptane(0.96), ethylbenzene(0.78), n-pentane(0.58) and n-hexane(0.43). A similar analysis of atmospheric reactivity ranking has been made recently for urban hydrocarbons [11], based on their median concentrations reported for 39 U.S. cities, i.e. ethylene(3.5), propylene(2.3), 1-butene(2.3), n-hexane(2.2), m, p-xylene(1.4), i-pentane(1.3), 1,2,4-trimethyl benzene(1.8), toluene(1.2), n-butane(1.0), methane(0.7), n-pentane(0.7) and o-xylene(0.5). It appears that the reactivity ranking is somewhat similar, at least qualitatively, for both the urban and rural anthropogenic hydrocarbons.

(III) Daytime Isoprene Concentration Versus Ambient Temperature

Isoprene is emitted primarily by deciduous trees during the daylight hours and, among various factors, its flux is most sensitive to the temperature at the leaf surface [12]. Thus, daytime concentrations of isoprene observed at the four ground sites are expected to be significantly influenced by ambient temperature and solar radiation. Quantitative relationships between natural NMHC source flux and ambient concentration are complex and involve accurate description of both mass transport and chemical production and loss terms. Under certain meteorological conditions a simple box model would provide a reasonable approximation [13,14]. Namely, the following simplified continuity equation describes the conditions that wind speeds are small and vertical mixing is controlled by the planetary boundary layer (PBL) mixing height:

$$(1/x)(dx/dt) = (Q/xh) - k$$

where x = spatial average concentration; Q = spatial average source strength; h = mixing height; k = first order rate constant for the loss of the trace gas; and t = time. This equation reduces to $x = Q/hk$ under a steady state condition, i.e. $dx/dt = 0$, and x is linearly dependent on Q when h and k are approximately constant. Such a situation may occur in the mid-afternoon under high pressure stagnation system. However, extensive data on diurnal mixing height and vertical profiles of natural NMHC concentrations are not available during this study period for all sites.

Site-to-site comparisons of isoprene concentration versus temperature have been made for all site, but only the results from Scotia and Dorset are presented below for illustrative purpose. Fig. 5 shows the Scotia data for sunny periods between 0800 and 1600 EDT, together with our data obtained at Dorset in 1989. The Scotia data represent the most extensive data set obtained at any of the four sites, and clearly demonstrates that the isoprene concentration increases exponentially by more than a factor of ten over the temperature range 15^{o} C to 35^{o} C. Available isoprene flux data for eastern U.S. deciduous trees indicate similar temperature dependence [15]. The 1989 Dorset data are also seen to exhibit similar temperature dependence, although generally lower in concentration than the Scotia data at a given ambient temperature. The isoprene data from Dorset in 1988 are plotted in Figure 6. The solid line in this figure corresponds to the least squares line from the Scotia data (Fig. 5) and the two parallel dashed lines are drawn to encompass all the Scotia data points. The 1988 Dorset data exhibit much larger scattering than those obtained in 1989, with no apparent dependence on wind direction. However, the upper limit values for these Dorset data are seen to coincide with the least squares line for the Scotia data, and the temperature dependence of the overall Dorset data is reasonably well represented by the lower bound line drawn for the Scotia data.

(IV) Correlation Among Anthropogenic NMHCs in Dorset Data

NMHC concentration/time profiles and their relative concentration distributions from the Dorset and Egbert data have been examined in detail to discern any observable trends and patterns indicative of source signatures and also to provide representative NMHC data corresponding to O_3 episodes as an input to the development of explicit chemical mechanism for oxidant modelling.

Summarized in Tables 2(A)-(C) are the values of rank correlation among various NMHCs (listed in Table 1) from Dorset data using Spearman method which is less sensitive to outliers than the more commonly used Pearson method. All the Dorset data are used to derive the correlation coefficients given in Table 2(A), whereas the morning, afternoon and night data were treated separately for the analysis shown in Tables 2(B)-2(C). The shaded boxes contain values ≥ 0.7 which were arbitrarily chosen as a cut off point to indicate a high degree of correlation. The highest correlation coefficient (0.97) in Table 2(A) is seen for n-C_5H_{12} and iso-C_5H_{12}, and this relation is illustrated graphically in Figure 7. Note that both n-C_5H_{12} and iso-C_5H_{12} are not only of combustion origin but also of similar atmospheric reactivity. In general, the light alkanes ($\leq C_6$) exhibit a fair degree of mutual correlation throughout the day. Figure 8 shows actual concentration/time profiles for C_2H_6, C_3H_8, n-C_4H_{10} and i-C_4H_{10} for the afternoon data. It was noted that these profiles for the light alkanes were also closely correlated with that of O_3. On the other hand, the olefinic and aromatic compounds are seen to be very poorly correlated irrespective of the time of the day. Although the exact cause(s) for this divergent behavior is not readily apparent, there are indications that the type and proximity of emission sources as well as atmospheric reactivity are among the probable contributing factors.

CONCLUSION

Data analysis of non-methane hydrocarbon compositions in the C_2-C_{10} range determined during the summer of 1988 at four rural sites in eastern North America, one in northern Georgia, one in central Pennsylvania and two in south-central Ontario, indicates that, although there are significant site-to-site variations of as much as a factor of 10 for some hydrocarbons in terms of median values, a high degree of similarity exists among the relative abundance of the hydrocarbons observed at all sites. The natural NMHC isoprene was the most abundant species in terms of ppbC among all NMHCs observed at all sites, and was primarily responsible for the local formation of oxidants. An extensive dataset for daytime isoprene concentrations at Scotia, Pennsylvania shows a well-defined exponential dependence on ambient temperature, providing a good reference for comparison with more limited isoprene data available from the other sites. Further temporary and spatially resolved data on both natural and anthropogenic hydrocarbons in representative Canadian rural settings are required for an assessment of regional oxidant problem.

ACKNOWLEDGEMENTS

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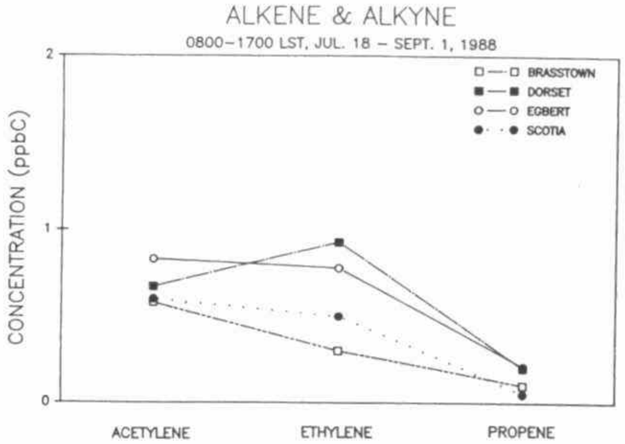


FIGURE 1

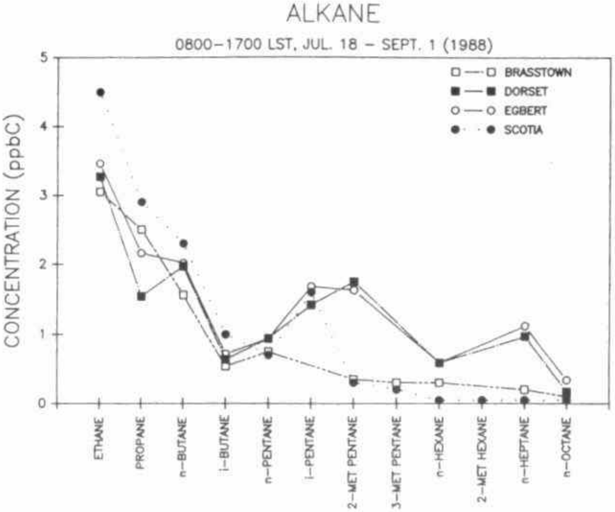


FIGURE 2

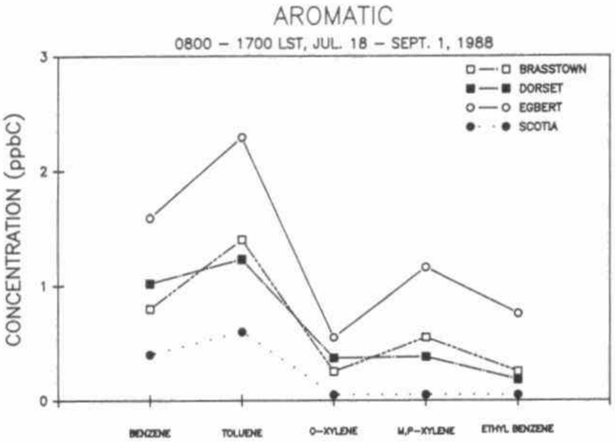
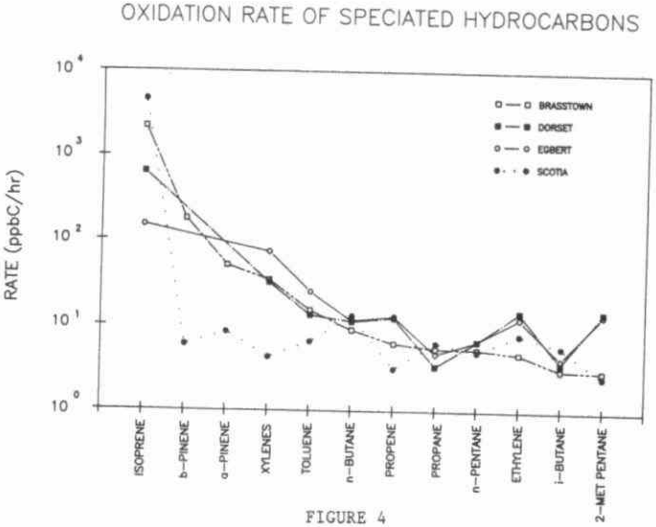


FIGURE 3



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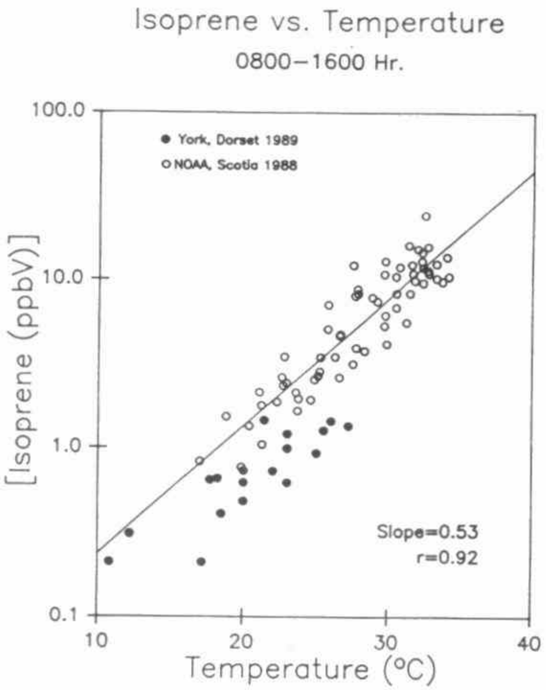

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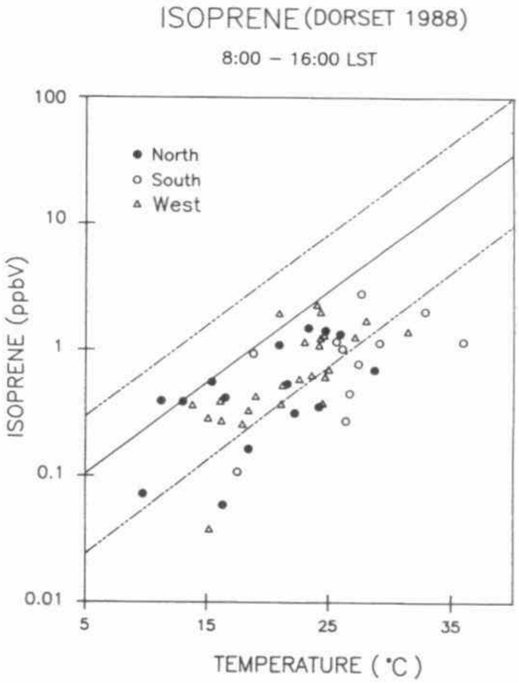

FIGURE 6

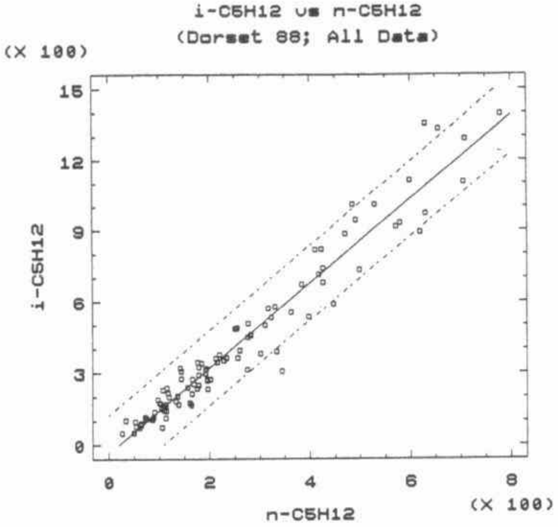

FIGURE 7

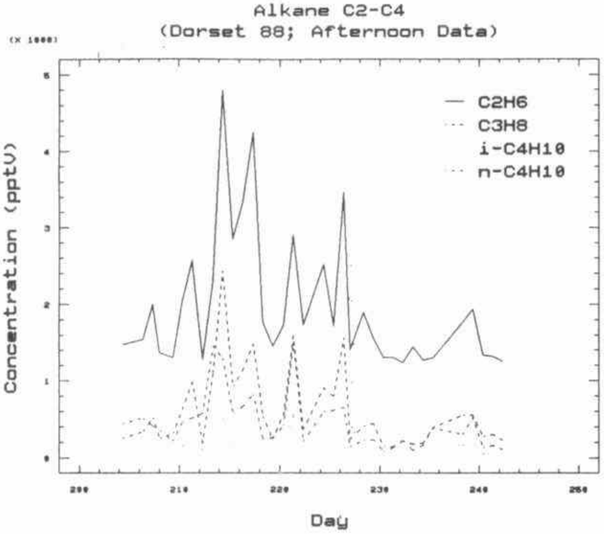

FIGURE 8

Table 1: SUMMARY OF SPECIATED HYDROCARBON CONCENTRATIONS AT RURAL SITES

1988 SUMMER EMEFS HC(ppbc, median) (all data 8:00-17:00 EDT)

Alkyne & Alkene	BRASSTOWN BALD	DORSET	EGBERT	SCOTIA
acetylene	0.58(0.86/0.36)	0.67(0.86/0.50)	0.83(1.29/0.57)	0.60(1.30/0.05)
ethylene	0.30(0.55/0.20)	0.93(1.25/0.70)	0.78(1.19/0.52)	0.50(1.50/0.20)
propene	0.10(0.30/0.10)	0.20(0.25/0.16)	0.21(0.30/0.18)	0.05(0.30/0.05)
Alkane				
ethane	3.05(4.30/1.20)	3.27(3.99/2.91)	3.46(4.78/2.98)	4.50(7.70/2.60)
propane	2.50(3.86/1.15)	1.54(2.21/1.17)	2.16(3.48/1.36)	2.90(5.40/1.30)
n-butane	1.56(2.98/0.91)	1.97(2.84/1.32)	2.02(3.01/1.35)	2.30(4.20/1.10)
i-butane	0.54(0.90/0.48)	0.64(0.99/0.44)	0.72(1.36/0.50)	1.00(1.90/0.40)
n-pentane	0.75(1.65/0.40)	0.94(1.28/0.72)	0.94(1.36/0.52)	0.70(1.30/0.40)
i-pentane		1.42(1.90/1.16)	1.68(2.59/0.83)	1.60(3.30/0.90)
2-met pentane	0.35(0.90/0.20)	1.75(2.20/1.92)	1.63(2.11/0.97)	0.30(0.70/0.05)
3-met pentane	0.30(0.65/0.15)			0.20(0.40/0.05)
n-hexane	0.30(0.50/0.20)	0.59(0.81/0.47)	0.59(0.87/0.40)	0.05(0.40/0.05)
n-heptane	0.20(0.45/0.10)	0.97(1.54/0.60)	1.12(1.72/0.64)	0.05(0.05/0.05)
n-octane	0.20(0.55/0.05)	0.17(0.34/0.12)	0.34(0.51/0.14)	0.05(0.05/0.05)
Aromatic				
benzene	0.80(1.25/0.55)	1.02(1.31/0.75)	1.59(2.68/0.98)	0.40(1.10/0.20)
toluene	1.40(3.05/0.90)	1.23(1.79/0.93)	2.29(3.92/0.78)	0.60(1.60/0.30)
o-xylene	0.25(0.60/0.15)	0.37(0.55/0.20)	0.55(0.78/0.37)	0.05(0.30/0.05)
p,m-xylene	0.55(1.40/0.30)	0.38(0.55/0.31)	1.16(1.84/0.55)	0.05(0.50/0.05)
ethylbenzene	0.25(0.50/0.15)	0.20(0.37/0.17)	0.76(1.10/0.68)	0.05(0.30/0.05)
Natural				
isoprene	12.20(25.70/3.20)	3.59(5.77/2.34)	0.84(1.47/0.59)	25.70(44.30/8.10)
α-pinene	0.30(25.70/3.20)			0.05(0.20/0.05)
β-pinene	1.50(4.95/0.25)			0.05(0.20/0.05)

Values in parentheses correspond to +/- 67 % of the data ranges.

TABLE 2(A) **RANK CORRELATION : Dorset 88 (All Data)**

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.46	0.71	0.47	0.77	0.63	0.70	0.57	0.62	0.54	0.62	0.24	0.20	0.04	0.29
C2H4	0.46	1.00	0.31	0.57	0.35	0.31	0.29	0.46	0.42	0.38	0.41	0.09	0.19	-0.08	0.25
C2H6	0.71	0.31	1.00	0.30	0.86	0.63	0.72	0.46	0.53	0.40	0.49	0.15	0.15	0.24	0.14
C3H6	0.47	0.57	0.30	1.00	0.39	0.49	0.43	0.64	0.60	0.54	0.51	0.25	0.29	-0.13	0.35
C3H8	0.77	0.35	0.86	0.39	1.00	0.76	0.85	0.64	0.70	0.52	0.61	0.21	0.35	0.14	0.38
n-C4H10	0.63	0.31	0.63	0.49	0.76	1.00	0.96	0.88	0.94	0.64	0.78	0.20	0.53	0.10	0.58
i-C4H10	0.70	0.29	0.72	0.43	0.85	0.96	1.00	0.83	0.90	0.63	0.76	0.22	0.50	0.12	0.51
n-C5H12	0.57	0.46	0.46	0.64	0.64	0.88	0.83	1.00	0.97	0.78	0.81	0.34	0.65	0.06	0.74
i-C5H12	0.62	0.42	0.53	0.60	0.70	0.94	0.90	0.97	1.00	0.74	0.84	0.29	0.61	0.07	0.71
n-C6H14	0.54	0.38	0.40	0.54	0.52	0.64	0.63	0.78	0.74	1.00	0.75	0.27	0.57	-0.01	0.52
i-C6H14	0.62	0.41	0.49	0.51	0.61	0.78	0.76	0.81	0.84	0.75	1.00	0.21	0.53	0.16	0.72
BENZENE	0.24	0.09	0.15	0.25	0.21	0.20	0.22	0.34	0.29	0.27	0.21	1.00	0.24	0.15	0.32
TOLUENE	0.20	0.19	0.15	0.29	0.35	0.53	0.50	0.65	0.61	0.57	0.53	0.24	1.00	0.38	0.63
o-XYL	0.04	-0.08	0.24	-0.13	0.14	0.10	0.12	0.06	0.07	-0.01	0.16	0.15	0.38	1.00	0.52
m,p-XYL	0.29	0.25	0.14	0.35	0.38	0.58	0.51	0.74	0.71	0.52	0.72	0.32	0.63	0.52	1.00

TABLE 2(B) **Dorset 88 (Morning Data)**

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.68	0.74	0.57	0.88	0.72	0.83	0.83	0.82	0.76	0.71	0.62	0.31	-0.02	0.25
C2H4	0.68	1.00	0.52	0.66	0.62	0.53	0.54	0.62	0.58	0.43	0.48	0.38	0.22	-0.04	0.22
C2H6	0.74	0.52	1.00	0.44	0.89	0.67	0.78	0.64	0.66	0.64	0.72	0.57	-0.06	0.37	0.24
C3H6	0.57	0.66	0.44	1.00	0.54	0.54	0.51	0.67	0.61	0.53	0.46	0.19	0.27	-0.04	0.16
C3H8	0.88	0.62	0.89	0.54	1.00	0.74	0.86	0.79	0.80	0.71	0.75	0.70	0.16	0.29	0.39
n-C4H10	0.72	0.53	0.67	0.54	0.74	1.00	0.94	0.91	0.95	0.69	0.82	0.64	0.36	0.01	0.56
i-C4H10	0.83	0.54	0.78	0.51	0.86	0.94	1.00	0.92	0.95	0.75	0.86	0.73	0.35	0.05	0.56
n-C5H12	0.83	0.62	0.64	0.67	0.79	0.91	0.92	1.00	0.98	0.76	0.80	0.70	0.48	-0.02	0.58
i-C5H12	0.82	0.58	0.66	0.61	0.80	0.95	0.95	0.98	1.00	0.75	0.84	0.71	0.45	-0.08	0.63
n-C6H14	0.76	0.43	0.64	0.53	0.71	0.69	0.75	0.76	0.75	1.00	0.81	0.47	0.37	0.01	0.49
i-C6H14	0.71	0.48	0.72	0.46	0.75	0.82	0.86	0.80	0.84	0.81	1.00	0.50	0.46	0.15	0.82
BENZENE	0.62	0.38	0.57	0.19	0.70	0.64	0.73	0.70	0.71	0.47	0.50	1.00	0.27	-0.09	0.18
TOLUENE	0.31	0.22	-0.06	0.27	0.16	0.36	0.35	0.48	0.45	0.37	0.46	0.27	1.00	0.01	0.51
o-XYL	-0.02	-0.04	0.37	-0.04	0.29	0.01	0.05	-0.02	-0.08	0.01	0.15	-0.09	0.01	1.00	0.46
m,p-XYL	0.25	0.22	0.24	0.16	0.39	0.56	0.56	0.58	0.63	0.49	0.82	0.18	0.51	0.46	1.00

TABLE 2(C) **RANK CORRELATION: Dorset 88 (Afternoon Data)**

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.29	0.74	0.41	0.85	0.72	0.81	0.55	0.69	0.54	0.69	-0.27	0.01	0.25	0.42
C2H4	0.29	1.00	0.20	0.58	0.18	0.30	0.27	0.41	0.42	0.58	0.38	-0.40	0.04	-0.02	0.17
C2H6	0.74	0.20	1.00	0.50	0.91	0.75	0.81	0.61	0.69	0.54	0.58	-0.14	0.02	0.47	0.23
C3H6	0.41	0.58	0.50	1.00	0.42	0.59	0.56	0.59	0.63	0.54	0.35	0.05	0.00	-0.25	0.18
C3H8	0.85	0.18	0.91	0.42	1.00	0.82	0.90	0.64	0.75	0.56	0.68	-0.31	0.30	0.41	0.49
n-C4H10	0.72	0.30	0.75	0.59	0.82	1.00	0.95	0.86	0.96	0.62	0.74	-0.41	0.40	0.00	0.77
i-C4H10	0.81	0.27	0.81	0.56	0.90	0.95	1.00	0.78	0.92	0.62	0.74	-0.33	0.34	0.51	0.75
n-C5H12	0.55	0.41	0.61	0.59	0.64	0.86	0.78	1.00	0.92	0.71	0.57	-0.40	0.34	0.20	0.72
i-C5H12	0.69	0.42	0.69	0.63	0.75	0.96	0.92	0.92	1.00	0.63	0.74	-0.40	0.34	0.49	0.79
n-C6H14	0.54	0.58	0.54	0.54	0.56	0.62	0.62	0.71	0.63	1.00	0.56	-0.31	0.42	0.23	0.18
i-C6H14	0.69	0.38	0.58	0.35	0.68	0.74	0.74	0.57	0.74	0.56	1.00	-0.54	0.18	0.41	0.41
BENZENE	-0.27	-0.40	-0.14	0.05	-0.31	-0.41	-0.33	-0.40	-0.40	-0.31	-0.54	1.00	-0.22	0.20	-0.25
TOLUENE	0.01	0.04	0.02	0.00	0.30	0.40	0.34	0.34	0.34	0.42	0.18	-0.22	1.00	0.57	0.56
o-XYL	0.25	-0.02	0.47	-0.25	0.41	0.00	0.51	0.20	0.49	0.23	0.41	0.20	0.57	1.00	0.80
m,p-XYL	0.42	0.17	0.23	0.18	0.49	0.77	0.75	0.72	0.79	0.18	0.41	-0.25	0.56	0.80	1.00

TABLE 2(D) **Dorset 88 (Night Data)**

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.36	0.66	0.33	0.63	0.71	0.75	0.53	0.63	0.55	0.50	0.24	0.26	-0.24	-0.13
C2H4	0.36	1.00	0.28	0.41	0.28	0.32	0.25	0.42	0.42	0.22	0.40	0.35	0.24	0.01	0.39
C2H6	0.66	0.28	1.00	0.01	0.77	0.68	0.76	0.40	0.53	0.32	0.32	0.01	0.39	0.01	0.07
C3H6	0.33	0.41	0.01	1.00	0.13	0.29	0.18	0.53	0.45	0.27	0.51	0.55	0.18	-0.10	0.35
C3H8	0.63	0.28	0.77	0.13	1.00	0.90	0.95	0.70	0.80	0.59	0.61	0.00	0.65	0.00	0.36
n-C4H10	0.71	0.32	0.68	0.29	0.90	1.00	0.97	0.84	0.93	0.67	0.78	0.02	0.68	0.15	0.52
i-C4H10	0.75	0.25	0.76	0.18	0.95	0.97	1.00	0.75	0.87	0.67	0.70	-0.04	0.67	0.06	0.42
n-C5H12	0.53	0.42	0.40	0.53	0.70	0.84	0.75	1.00	0.96	0.81	0.96	0.29	0.81	0.07	0.79
i-C5H12	0.63	0.42	0.53	0.45	0.80	0.93	0.87	0.96	1.00	0.74	0.92	0.16	0.81	0.27	0.67
n-C6H14	0.55	0.22	0.32	0.27	0.59	0.67	0.67	0.81	0.74	1.00	0.81	0.16	0.76	-0.27	0.57
i-C6H14	0.50	0.40	0.32	0.51	0.61	0.78	0.70	0.96	0.92	0.81	1.00	0.22	0.74	0.11	0.75
BENZENE	0.24	0.35	0.01	0.55	0.00	0.02	-0.04	0.29	0.16	0.16	0.22	1.00	0.05	-0.12	0.13
TOLUENE	0.26	0.24	0.39	0.18	0.65	0.68	0.67	0.81	0.81	0.76	0.74	0.05	1.00	-0.03	0.65
o-XYL	-0.24	0.01	0.01	-0.10	0.00	0.15	0.06	0.07	0.27	-0.27	0.11	-0.12	-0.03	1.00	0.51
m,p-XYL	-0.13	0.39	0.07	0.35	0.36	0.52	0.42	0.79	0.67	0.57	0.75	0.13	0.65	0.51	1.00

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ATMOSPHERIC TRACE GAS MEASUREMENTS USING A TUNABLE DIODE LASER ABSORPTION SPECTROMETER

H. I. Schiff*, R. Berman, D. R. Hastie, and S. Sharma

Department of Chemistry
and
Centre for Atmospheric Chemistry,
York University

INTRODUCTION

The Eulerian Model Evaluation Field Study (EMEFS) was designed to provide sufficient data to allow a full evaluation of computer models of the atmosphere over Northeastern North America. The major thrust was in the evaluation of the two state-of-the-science Eulerian models being used to simulate and study the chemistry of acid deposition and oxidant formation. They are the Acid Deposition and Oxidants Model (ADOM) (Venkatram et al. 1988), supported by the Ministry of the Environment, the Atmospheric Environment Service of Environment Canada, the Electric Power Research Institute (EPRI), and Umweltbundesamt (West Germany) and The Regional Acid Deposition Model (RADM) (Chang et al. 1987) supported by the Environmental Protection Agency (EPA). These models include our current best understanding of the sources of gases to the atmosphere, the best available three dimensional meteorology, the most complete gas and aqueous phase chemistry available, and our best measurements of trace gas concentrations. Realizing the importance of the predictions of these models, it was deemed necessary to establish their credibility by comparison with data collected during EMEFS.

The Canadian component of the field study involved data collection from the MOE-APIOS and AES-CAPMoN networks. In addition, two sites were designated as intensive or enhanced sites. These were the AES site at Egbert (near Barrie) and the Ministry site at Dorset. The purpose of these sites was to obtain data using enhanced techniques that required operation by specially trained personnel or at a frequency not possible under normal operating conditions.

While the field study was put in place for model evaluation it became clear that the data obtained, especially that from the enhanced sites, could also be used to address a number of additional issues. The Canadian Institute for Research in Atmospheric Chemistry (CIRAC) took the lead in the co-ordination of the Canadian Air Chemistry Experiment (CACE) which aimed to ensure the collection of a complete data set capable of addressing some specific atmospheric chemistry questions. The work performed under this grant had as its focus the EMEFS program but we were always mindful of the objectives of CACE.

We undertook a measurement program at the Ministry site at Dorset to measure the concentrations of a number of key species in the atmospheric oxidation cycle. In this paper we use some of the data obtained, during a field campaign in the summer of 1989, to investigate the importance of some site specific effects on the chemical composition of the atmosphere. The ability to distinguish between such local effects and larger scale changes in atmospheric composition is necessary if we are to continue to improve our understanding of the chemistry of the atmosphere.

MEASUREMENTS

The following is a listing of the chemical species that were measured at the Dorset site, and a brief description of the techniques used.

Hydrogen Peroxide and Formaldehyde using a Tunable Diode Laser Absorption Spectrometer (Schiff et al. 1983, 1987, Harris et al 1990, and Slemr et al. 1986)

NO and NO_y using an in-house fabricated, high sensitivity chemiluminescent NO analyzer similar to that used by Misanchuk et al. (1987). This was equipped with a gold converter for NO_y measurements (Fahey et al. 1986).

Ozone using a commercial UV absorption ozone analyzer (Dasibi Model 1003-AH).

NO_2 and NO_x using two modified commercial luminol NO_2 analyzers (Unisearch/Scintrex LMA-3) to measure NO_2 directly and NO_x ($NO + NO_2$) by use of a CrO_3 converter (Drummond et al. 1990).

Solar radiation using a U.V. radiometer (Eppley Labs 280-320nm).

Basic meterological parameters using a commercial meteorological system (MetOne) for wind speed, wind direction, temperature and humidity.

Boundary layer heights up to 500 meters were obtained by Ontario Hydro using an acoustic sounder.

CASE STUDY: THE NIGHT OF JULY 2 1989

We have chosen this night as the case study as the two days seem to be similar and there is a clear nocturnal inversion leading to some interesting observations.

There was a stable high pressure system over the site. The daytime temperature maximum for both days was 29°C with the nighttime minimum of 9°C. The radiation measurements for both days showed they were relatively cloud free. The wind velocities during the daylight hours were stable at around 4-6 km/hr from the west, but dropped to below 1 km/hr and shifted to be almost from the north for most of the night.

As expected under these conditions a strong nighttime radiation inversion was formed. The acoustic sounder first indicated a developing inversion at 1945. By 2215 this had developed into a very strong stable surface based inversion whose depth varied from 80 to 200 meters with an average of 150 meters. The lower temperature and trapping of the air close to the surface brought relative humidities to the saturation level as evidenced by our sensor recording relative humidities over 100%

for the duration of the strong inversion. This inversion began to lift at 0915, three hours after first light. There was evidence of a 200 meter thick rising dissipating elevated inversion for an additional next half hour before the inversions finally dissipated and the normal daytime thermal activity dominated the first 500 meters of the atmosphere.

Knowing the height of this nocturnal inversion is extremely important in interpreting data from this site. It is in a shallow valley with hills within a kilometre in three directions. The highest points on each of these hills are 67, 69 and 89 meters above the site. These data show that the nighttime inversion reaches above these hills so the site is not completely isolated at night. There is still the possibility of horizonal transport under the inversion although in this case the low wind speeds would preclude very much transport. This sounder data is supported by a single night of ozone measurements where the ozone measured on the top of the highest hill was identical to that measured at the site. Thus we must conclude that the nighttime measurements made at the site are representative of the surface for the surrounding area.

The chemical and meteorological data are plotted in the Figures. Figure 1 shows the height of the inversion and the U.V. solar irradiance. The inversion developed slowly after U.V. sunset and persisted well after sunrise. The very low heights in the early evening were from the weak developing inversion, the strong inversion commenced at about 10 pm. Figure 2 shows the relative humidity and wind speed data. High humidities and low wind speeds were associated with the strong inversion. Thus the aqueous phase become increasingly important and the amount of horizontal transport was small.

Figure 3 shows the NO_x and ozone data. Ozone showed a strong diurnal variation. The maximum concentration for both days was 90 ppbv a value indicative of strong photochemical activity. The concentration began to fall at 1945 coincident with the onset of the inversion. The concentration droped all night to a minimum of 25 ppbv at 0445 but when the inversion broke up at 915 the ozone rose quickly and when the last of the inversion dissipated at 0945 the ozone concentration was back up to 68 ppbv and reached 80 within half an hour. The ozone trapped below the inversion was clearly lost during the night whereas the ozone aloft, which was mixed back to the surface following the breakup of the inversion, was not. The ozone could have been lost by reaction or deposition to the surface. There was no indication of an NO source in the area and the emission of reactive hydrocarbons at these low temperatures is expected to be low thus deposition to the surface is the most likely fate of the ozone. The ozone concentration shows an exponential decay and if we assume an inversion depth of 150 meters, the deposition velocity calculated from the decrease in ozone over the 9 hours of the inversion is $0.55 \pm .02$ cm s^{-1}. This is consistent with the commonly accepted value of approximately 0.5 cm s^{-1}. NO_x, the sum of NO and NO_2 showed a similar decay to that of ozone indicating a similar deposition velocity.

Hydrogen peroxide and formaldehyde are shown in Figure 4. Hydrogen peroxide, which had averaged 2 ppbv during the afternoon, dropped precipitously as the inversion formed. This removal was too fast to be a surface process and was more likely an absorption of hydrogen peroxide into the rapidly growing aqueous phase as the temperature dropped and the humidity increased. The hydrogen peroxide appeared again with the breakup of the inversion bringing dryer air from aloft. Formaldehyde exhibited a complex behaviour as it appeared to increase as the inversion formed and there was some deposition loss with a deposition velocity of about 0.2 cm s^{-1}. The concentration rose again as the inversion broke up.

CONCLUSION

We have identified a night in which there was a strong nocturnal inversion and that this had some interesting chemical consequences. We are able to use them to examine both physical and chemical processes that are occurring. The data could now be compared directly with nocturnal boundary layer models. Finally the removal of such local effects will ensure the remaining data will be representative of the region and provide a good data set against which to evaluate models.

ACKNOWLEDGEMENT

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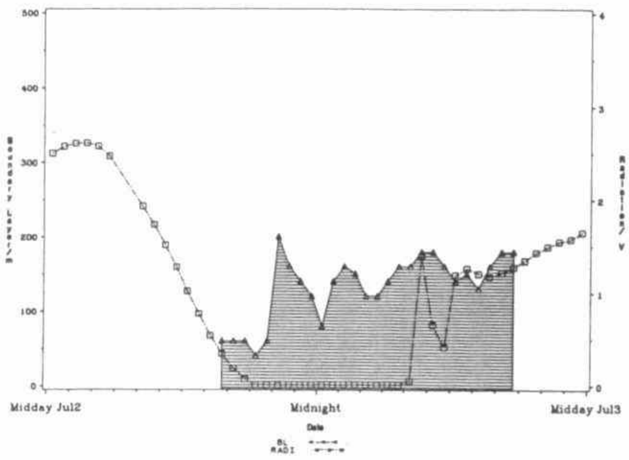

FIGURE 1: U.V. Radiation and boundary layer height as measured at the Dorset site on the night of July 2 1989.

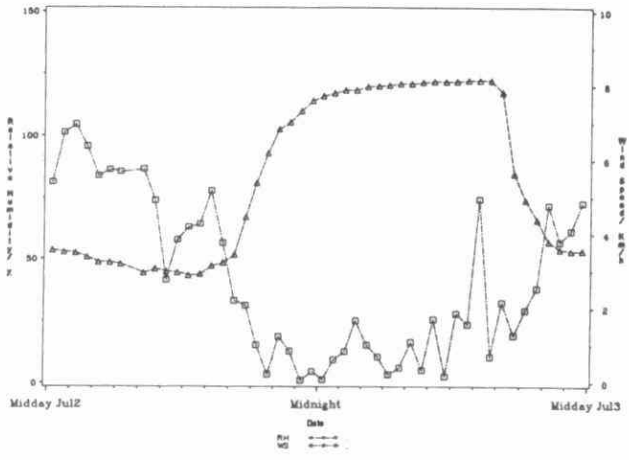

FIGURE 2. Relative Humidity and Wind Speed measured for the same conditions as Figure 1

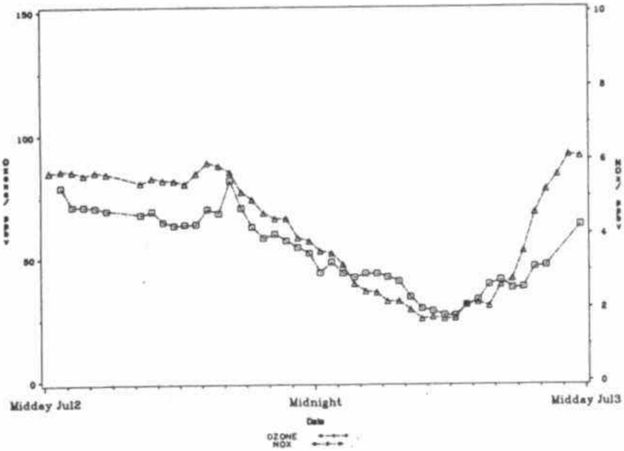

FIGURE 3: Ozone and NO_x as measured for the same conditions as Figure 1

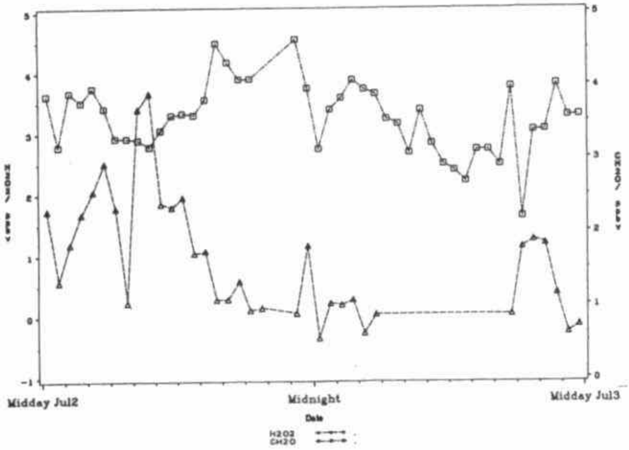

FIGURE 4: Formaldehyde and Hydrogen Peroxide as measured for the same conditions as Figure 1

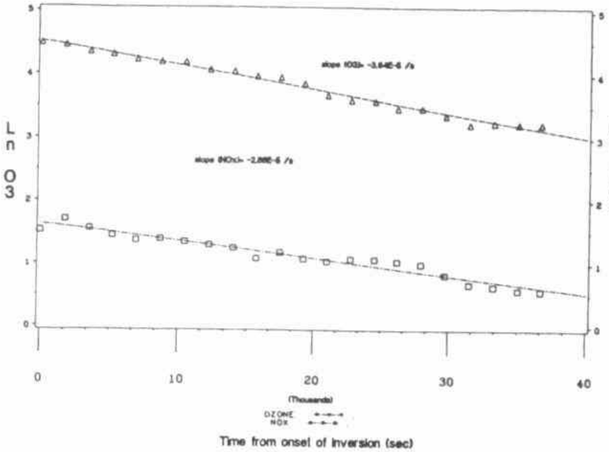

FIGURE 5: Regression plots of Ln(ozone) and $\ln(NO_x)$ against the duration of the strong nocturnal inversion.

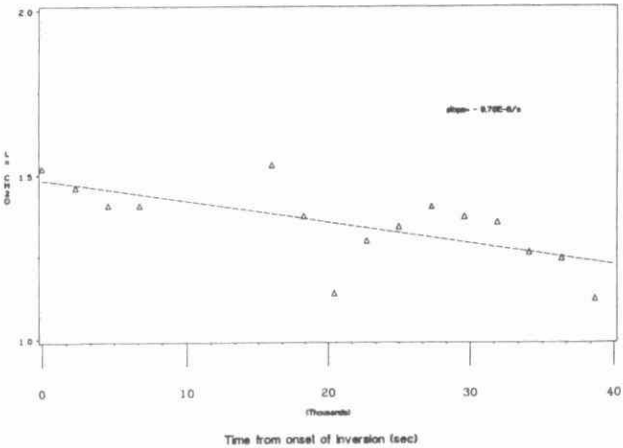

FIGURE 6: Same as Figure 5 but for formaldehyde.

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UPTAKE AND DISTRIBUTION OF NAPHTHALENE IN VEGETABLE PLANTS FOLLOWING FOLIAR AND ROOT EXPOSURE

B. Hale-Marie and D.P. Ormrod

Department of Horticultural Science
University of Guelph
Guelph, Ontario
N1G 2W1

Abstract

For the purposes of risk analysis, it is desirable to determine dose-response relationships describing the growth response to and tissue accumulation of organic pollutants, relative to various environmental parameters. This paper describes preliminary results of a study, the objectives of which are to relate foliar and root exposures of various vegetable species to naphthalene/naphthol, to growth and tissue concentration responses, as they relate to soil type. This study utilizes a central composite factorial experimental design and analysis of covariance to enhance the collection and interpretation of data. The first experiment demonstrated that growth response to naphthol was more strongly related to soil type (as described by cation exchange capacity) than to applied concentration. Regression analysis indicated that the shape of the response was positive linear and negative quadratic, indicating that as CEC increases, growth reduction by soil naphthol is increasingly diminished. An experiment into plant response to atmospheres containing naphthalene suggests that species type is a strong determinant of tissue accumulation; these results however, are very preliminary and require confirmation.

Introduction

The phytotoxicity and potential for contamination of vegetables by organic compounds of industrial origin is of increasing concern to members of both public and private sectors. While a considerable data base on the uptake and accumulation of agricultural organic chemicals by vegetation exists, a similar data base for industrial organic compounds is scanty. The information on agricultural chemicals cannot be readily transferred to industrial contaminants, as the molecular characteristics of the two groups of compounds are quite different. The uptake of organic compounds from soil or air by plants is dependent on numerous parameters, including the size and water solubility of the compound, and the tendency of the compound to adhere to soil particles. This latter characteristic is to a large extent dependent on the soil type, in particular the amount of organic material, and the relative tendency of a soil to sequester organic molecules may be indicated by the cation exchange capacity (CEC). Due to the wide range of soil types which may be encountered in a natural or agricultural ecosystem, it is desirable that dose-response relationships be developed to describe the response of plants to ranges of contaminant concentration and soil types. The objectives of this project are to determine dose-response expressions which relate concentration of naphthalene or naphthol applied to the soil or the air surrounding the plant and cation exchange capacity of the rooting medium, to growth and tissue naphthalene concentration of tomato (*Lycopersicon esculentum* cv. New Yorker), radish (*Raphanus sativus* cv. Cherry Belle) and swiss chard (*Beta vulgaris* cv. White King). The dose response relationships are to be determined using: an incomplete factorial experimental design known as a partial central composite; analysis of covariance for the reduction of plant-to-plant variation; and polynomial regression for description of the relationship (Marie and Ormrod, 1986; Ormrod *et al.*, 1984).

Materials and Methods

Seeds were sown in either Promix BX (high cation exchange capacity), a mixture of sand and Promix BX (low cation exchange capacity) or a mixture of vermiculite and Promix BX (medium cation exchange capacity), at a rate of three seeds per pot. The pots were then placed in a controlled environment chamber which delivered a day/night temperature regime of 25/20°C, each for 12h, canopy level photosynthetically active radiation at 325 $\mu E\ m^{-2}s^{-1}$ for a 16h photoperiod and 70% relative humidity (Ormrod *et al.*, 1980). Planting was staggered in order that germination of all three species occurred on approximately the same day. Three days after germination, seedlings were thinned to one per pot, and the plants were grown for three more weeks. During this period, they were irrigated with half-strength Hoagland's nutrient solution as required, when the soil appeared dry. On day 22, planar leaf area of swiss chard and radish, and plastochron index of tomato, were estimated for use in analysis of covariance.

Following covariate measurement, the plants were placed in exposure cubes with environmental conditions similar to those in the controlled environment growth chambers. Two ml of naphthol or naphthalene in ethanol were applied to the soil; plants were harvested on the third day after application of the contaminant. Foliar injury, as well as fresh and dry weights of shoot (divided into stem, leaf and hypocotyl where applicable) and leaf area were assessed on the plants. Exposure of shoots to air containing naphthalene was accomplished by constructing large permeation tubes through which air was passed and then metered into the main air stream entering the exposure chambers. Alteration of the rate of air flow through the permeation tube with a flowmeter controlled the concentration of naphthalene in the chamber. Determination of exposure concentration was by gas chromatography, using manual injection; samples were taken hourly during the five days of exposure. At the end of the exposure, analysis of naphthalene concentration in plant tissues was determined; since the tissue was not washed prior to analysis, the values represent surface adsorption as well as absorption.

The experimental design was a partial central composite, with seven contaminant concentration/soil CEC combinations (Figure 1). The central treatment (CEC=med, naphthol/naphthalene concentration=10 mg/l) is repeated twice for each replication of the other points, in order that all areas of the response surface have approximately equal estimates of variance. The treatment means were summarized by polynomial functions in the second order for both factors, including an interaction term.

Results

Preliminary results (first two of four replications) indicated that there was differentiation among the treatment means for each species exposed to naphthol via the soil (Table 1). When the data (which are summarized in Table 1) were subjected to regression analysis, most growth parameters were related to CEC more strongly than to concentration of naphthol (Table 2). For all growth parameters, a significant portion of the total sum of squares was accounted for by the covariate, indicating that a significant reduction in error sum of squares was realized, leading to improved precision of the experiment (data not shown). This contribution of analysis of covariance to the detection of plant response has been noted for gaseous air pollutant studies (Ormrod *et al.*, 1983). Also not shown are the data for growth response of radish hypocotyl and tomato stem, for which there was little of significance, mainly due to large variation in the data. It should also be noted that naphthalene caused very little growth response in these three species, likely due to its low solubility in water; those results are not reported here.

Tissue concentrations of naphthalene from the first replication of the experiment in which the plant shoot was exposed to atmospheres containing various concentrations of naphthalene, demonstrated no consistent effect of soil type, but were related to exposure concentration and species (Table 3). Tomato shoot had the highest tissue concentrations of naphthalene at all exposure concentrations, while the other two shoot types had similar tissue concentrations, relative to exposure concentration. Radish root data were similar to that for radish shoot.

Discussion

Although Table 1 indicates that both concentration of naphthol and cation exchange capacity of the rooting medium are related to growth response of these species to this compound, it is clear from the regression analysis in Table 2 that CEC is the more important determinant of growth response to naphthol in the soil, and that there is little interaction between these two factors in those responses. This suggests that the concentration of compound available to the plant is determined more by soil type than by the applied dose, within the ranges of the two factors utilized in this study. Finalization of the dose response relationships, in the form of quantification of the polynomial coefficients, will further characterize the relative importance of the linear and quadratic components. When plant shoots were exposed to atmospheres containing naphthalene, tissue concentration was independent of soil type, as could be expected. However, it was related to exposure concentration and plant species; this latter factor probably relates to the affinity of the leaf surface for the compound (i.e. the presence of trichomes or cuticular waxes). It is clear from these data that greater separation of treatment concentrations is required for the establishment of dose-response relationships.

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Figure 1: Treatment combinations for partial central composite rotatable experimental design.

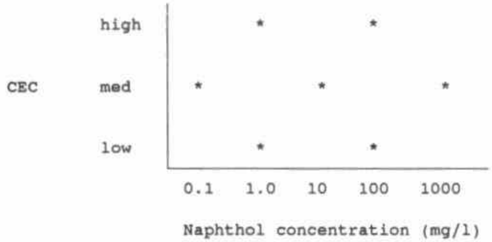

Table 1: Treatment means for growth response of tomato, radish and swiss chard grown in rooting media with different CEC's, to various concentrations of naphthol.

CEC	low		med			high	
[nap]	1.0	100	0.1	10	1000	1.0	100
Tomato							
LFW	2.27	2.43	3.16	2.39	1.76	2.67	2.08
LDW	.211	.251	.305	.240	.216	.249	.232
LA	87.8	94.7	118	90.3	60.7	101.3	74.9
Radish							
LFW	3.96	4.12	6.95	5.35	4.63	6.04	5.22
LDW	.416	.409	.554	.452	.533	.432	.468
LA	107	111	174	141	124	161	142
Swiss chard							
SFW	3.21	2.25	4.16	5.29	1.66	4.05	3.61
SDW	.246	.263	.306	.334	.220	.272	.299
SA	64.0	48.2	84.0	102	46.9	83.3	76.9

LFW and LDW are leaf fresh and dry weights, respectively, the units of which are g/plant. SFW and SDW are shoot fresh and dry weights, respectively, the units of which are g/plant. LA and SA are leaf and shoot area, respectively, the units of which are cm^2/plant.

Table 2: Polynomial coefficients which describe the relationships between growth of tomato, radish and swiss chard, and CEC of rooting media and concentration of naphthol.

	CEC	[nap]	CEC x [nap]
Tomato			
LFW	+L, -Q	ns	-
LDW	+L, -Q	ns	ns
LA	+L, -Q	ns	ns
Radish			
LFW	+L, -Q	ns	ns
LDW	+L, -Q	ns	ns
LA	+L, -Q	ns	ns
Swiss chard			
SFW	+L, -Q	ns	ns
SDW	+L, -Q	+L, -Q	ns
SA	+L, -Q	ns	ns

+L indicates linear coefficient with a positive sign;
-Q indicates quadratic coefficient with a negative sign;
- indicates negative interaction;
ns indicates no significant regression coefficients;
linear and quadratic coefficients significant at $P \leq 0.10$.

Table 3: Treatment means for tissue concentration of tomato, radish and swiss chard grown in media with different CEC's and exposed via the atmosphere to various concentrations of naphthol.

Species Soil Type	Exposure Concentration (ng/cc) 12	 14	 19	 65
Swiss Chard shoot				
P + S	.03	.01	.03	.16
P + V	.02	.02	n.d.	.11
P	.06	.06	.04	.18
Tomato shoot				
P + S	.48	.26	n.a.	2.20
P + V	.42	.25	.16	2.30
P	.14	.22	.21	1.10
Radish shoot				
P + S	.09	.03	.03	.16
P + V	.04	.03	.21	.30
P	.05	.03	.05	.30
Radish hypocotyl				
P + S	.02	.01	.02	.10
P + V	.02	n.d.	.02	.11
P	.05	n.d.	n.d.	.13

P + S indicates Promix/sand mixture;
P + V indicates Promix/vermiculite mixture;
P indicates Promix used alone;
n.d. indicates below limit of detection;
n.a. indicates not available

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PHYTOTOXICITY OF URANIUM

S.C. Sheppard, W.G. Evenden and A.J. Anderson
Environmental Science Branch,
AECL Research, Whiteshell Laboratories
Pinawa, Manitoba R0E 1L0

ABSTRACT

The literature offers conflicting information on the phytotoxicity of uranium (U). Levels as low as 5 mg U/kg soil, well within the normal background range, have been cited as toxic, whereas many studies report no toxicity at levels 100- to 1000-fold higher. Uranium in soil does not often present a radiological hazard to humans, but toxicity to plants could lead to prescribed cleanup and assessment criteria for industrial activities. This study was designed to identify the concentration of soil U at which plant performance is affected. Although the results here are expressed relative to total soil U, measures of soil-extractable U and plant U concentrations are pending. Nine levels of U were added to background-level soils. Beans were grown to maturity in an outdoor lysimeter study with two soils. Germination tests in the growth chamber were done with eleven soils and with five plant species. A rapid cycling *Brassica rapa* cultivar, proposed as a new toxicity test subject, was also grown to maturity on two of the soils in the growth chamber. Preliminary observations indicate little or no effect of concentrations below 300 mg U/kg soil. Results from the seed germination experiments only are presented in this preliminary report.

INTRODUCTION

A recent literature review highlighted the deficiencies of data on uranium (U) toxicity to plants (Sheppard 1989). Several papers reported toxicity at near background levels, below 10 mg U/kg soil. The concern with these papers, although they have been cited by various agencies (Hanson 1980, Inland Waters Directorate 1983, Beak Consultants Ltd. 1987), is that their findings are difficult to confirm. One is a review of German research prior to 1927 (Stoklasa and Penkava 1928), and interpretation is made difficult by the use of archaic units of measure and uncertain methods. The others are more recent (Zhukov and Zudilkin 1971, Bufatin et al. 1986, Shevchenko et al. 1987) and describe what appear to be reasonable pot culture experiments. However, interpretation is again hampered by the lack of ancillary information. In contrast to these, there are numerous, better-supported reports of no toxic effects at much higher U levels (see Sheppard 1989).

This discrepancy in the literature must be resolved. At present it is not clear whether U toxicity to plants occurs at the concentrations found in some Ontario soils. Phytotoxicity of U may be an important criteria for remediation in areas such as around Port Hope. As a result, this study was undertaken.

The results presented in this report do not include the entire study. In particular, results from the outdoor, full maturity experiment, and of U analyses in soils and plants, are pending.

METHODS AND MATERIALS

Soil Collection, Preparation and U Analyses

Eleven soils were chosen to represent a broad range of edaphic variables (Table 1), and to represent background-level soils from regions in Canada where high levels of soil U are found. About 600 L of the agricultural (A), boreal forest (B) and garden (G) soils, and 60 L of the other soils, were collected. They were partially dried to a workable moisture content and sieved to pass a 0.5-cm mesh. After thorough mixing, each soil was stored in sealed plastic pails. Whenever soil was taken from these pails, the moisture content was determined, and all analyses and treatments were based and are presented on an oven-dried moisture content (105°C for 24 h).

TABLE 1

Properties of the soils used in the study, indicating also the region or important feature each represents and the background U concentrations.

Soil	Region or feature[1]	Texture[2]	Bkgd.U (mg/kg)	Clay (%)	CO_3[3]	CEC[4] (cmol /kg)	Organic matter (%)	Available P (mg/kg)
A	PH	L	2.1	24	a	14.4	2.2	5.0
1B	limed sand	fine S	0.6	2	a	11.0	1.0	17.0
G	garden	fine SL	3.1	18	vl	50.5	18.4	8.6
uB	acid sand	fine S	0.6	2	a	5.4	0.7	10.6
E	EL sand	LS	4.1	6	vl	17.0	3.5	1.6
X	PH medium	fine SL	2.1	15	vl	13.0	2.6	19.6
Y	PH light	L fine S	1.5	4	a	4.4	0.8	6.0
Z	PH organic	fine SL	1.8	13	a	19.9	5.7	40.6
#1	clay	CL	2.1	33	a	24.1	3.1	14.0
#2	carbonated	fine SL	2.1	12	l	17.8	4.2	9.6
#4	organic	O	4.9	<1	a	81.4	41.5	48.0

[1] The regions are PH (Port Hope, Ontario) and EL (Elliot Lake, Ontario).

[2] Symbols denoting texture are C (clay), L (loam), O (organic) and S (sand).

[3] Carbonate content was qualitatively assessed, based on reaction to drops of HCl as: a (absent, typically <0.1% CO^3), vl (very low) and l (low, about 1% CO_3).

[4] CEC stands for cation exchange capacity.

The B soil was too acidic for many crops, but was important as a representative of boreal forest settings. Therefore, it was used both limed and unlimed, designated as 1B and uB, respectively. The liming rate was determined by a 2-week incubation study, as well as previous experience with this soil. After application of 0.5 g $CaCO_3$/kg, the pH was raised to about 6.5. The edaphic variables listed in Table 1 were determined following standard procedures by the Manitoba Provincial Soil Testing Laboratory and the Saskatchewan Research Council.

Uranium Treatments, Replication and Statistical Analyses

The emphasis of this study was on U concentration levels found as extremes in the environment, but higher levels were included to ensure correct interpretation of symptoms and other effects. An optimized matrix of U levels and replication was used in each part of the study. The levels, as mg U/kg soil, and in brackets the number of replicates, were 0(4), 3(1), 10(2), 20(3), 30(3), 50(3), 100(2), 300(1) and 1000(1). This gave a total of 20 treatment/replicate units. This matrix was repeated for each crop and soil combination in each of the experiments.

Interpretation throughout was guided first by a segmented regression, which identified apparent toxicity thresholds, and then by analyses of variance using the general linear model (GLM) of SAS (1985). The segmented regression was iteratively fit so that at U levels below a threshold (TU), the response (Rs) was defined as a constant (C); and at U levels above TU, Rs was a decreasing linear function of U level with slope -b; as follows:

if $U < TU$, then $Rs = C$

if $U >= TU$, then $Rs = C - b(U - TU)$

Bounds were set to limit b to negative values. When a value of TU could not be resolved, the iterative process found b = 0 and/or TU beyond the range of our treatments. When a value of TU was resolved, it was an effective, unbiased indicator of a toxicity response pattern. Once this pattern was identified, tests of individual means, at levels beyond TU, versus controls were done as one-tailed, single-degree-of-freedom contrasts. The bounds on b and the use of one-tailed tests arises from rejecting hormesis as a valid hypothesis in this study.

The uranium was acquired as (natural, undepleted with respect to ^{235}U) uranium oxide powder and was dissolved in a minimal amount of concentrated nitric acid. In order to ensure that nitrogen (N) supply did not interfere with results, the N applied in each treatment below the 100 mg U/kg level was adjusted using NH_4NO_3 to the N level of the 100 mg U/kg treatment. As a result, treatments above the 100 mg U/kg level had more N than the lower treatments. It was inappropriate to elevate all treatments to very high, but uniform, N levels, as this would have been atypical of normal garden or agricultural settings.

Soil Range Experiment

All 11 soils were used in the soil range experiment, in order to examine the effect of edaphic factors on U toxicity. The soils included the A, 1B, and G soils used in the full maturity experiment (not reported here), the unlimed B soil (uB), soils representative of Elliot Lake (E) and

Port Hope (X, Y, Z), Ontario, and soils used by Sheppard et al. (1989) (#1, #2, #4) in a previous experiment with U (the uB soil was used by Sheppard et al. as their #3 soil). Aliquots of 450 mL of soil were placed in 1-L plastic containers. The U, nitrogen and lime were added, the soils thoroughly mixed and the soil transferred to 500-mL plastic containers. Bean seeds previously selected for weight uniformity were sown at 25 per container, 1 cm below the soil surface. The soils were wetted to 90% of field capacity, and the containers sealed and incubated at 20°C for 10 d. The numbers of germinated seeds were recorded.

Plant Species Experiment

This experiment measured germination of corn, lettuce, tomato, short-life-cycle Brassica rapa and white pine. The G and 1B soils were used, and 2.25-L aliquots were treated in 5-L plastic containers. These aliquots were then split into five, 500-mL plastic containers and the seeds sown. We sowed 25, 100, 100, 25 and 50 seeds per pot for each of the crops, respectively.

In addition to the treatment/replicate schedule used in the other experiments, we included several series of further treatments for the B. rapa only. The U treatments were increased to include duplicates of 300, 1000, 3000 and 10000 mg U/kg. Also included were two other series of duplicated treatments, one with 10, 20, 30, 50 and 100 mg As/kg and the other with 50, 100, 300, 600 and 1000 mg Zn/kg. The As was applied as solutions of $Na_2HAsO_4.7H_2O$ and the Zn as solutions of $ZnSO_4.7H_2O$.

Final emergence counts were recorded for all crops, and several intermediate counts were possible for the pine. The corn seedlings were retained and dry weights determined.

The pots containing B. rapa were thinned to six plants and the plants grown to maturity in the growth chamber. Effects of U on yield at maturity and on second generation seed germination will be available in later reports.

RESULTS AND DISCUSSION

The toxicity of U did not vary substantially among the soils of the soil range experiment, and there was no overall toxicity (Table 2). A few treatments had means significantly below the controls, but most of these did not conform to a smooth, continuous response curve as expected in a concentration series study. Given the probability level of P=0.05, a false conclusion rate of one-in-twenty statistical contrasts is expected, and this may account for these occasional, spurious indications of significance. There was a significantly lower germination in the #1 soil, and the regression analysis also showed a threshold level (at 530 mg U/kg) in this soil. Thus, toxicity was apparent in this soil. However, it is not clear why toxicity would have been more acute in this soil compared to the others. This soil is a high-pH, clay loam that strongly sorbs U (Sheppard et al. 1989). Perhaps even this result is attributable to the statistical error rate. There were several cases of decreased germination

TABLE 2

Germination (%) of bean in 11 soils as effected by U[1]

Soil	Control[2] (n=4)	Uranium treatment (mg U/kg) 10 (n=2)	20 (n=3)	100 (n=2)	300 (n=1)	1000 (n=1)
A	97 TU	96	96	96	88	92
1B	96 TU	98	96	96	96	92
G	76	82	79	60	80	96
uB	98 TU	94	99	98	100	92
E	98	96	99	96	92	100
X	74	70	69	92	92	48
Y	99	96	95	94	100	100
Z	93	74 *	93	98	96	100
#1	85 TU	74	95	84	88	48 *
#2	86	82	63 *	92	24 *	92
#4	90 TU	80	67 *	72 *	52 *	72

[1] Only controls and those U concentrations where at least one value was significantly different from the corresponding controls are shown. Significance relative to the controls (i.e. within each row) is indicated by * and is based on one-tailed, single-degree-of-freedom contrasts with $P<0.05$.

[2] Control values followed by 'TU' are of soils where segmented regression showed a threshold U concentration; beyond the threshold, germination percentages showed a decreasing trend.

in the #4 soil, but there was no decrease at 1000 mg/kg. This soil was organic and, because of the strong retention of U observed in organic soils, it is the most unlikely soil type in which toxicity might occur.

When crops other than beans were investigated, toxic effects were more apparent (Table 3). In the B soil, all crops had significantly reduced germination at 1000 mg U/kg, and threshold values were indicted by the regression analyses. The thresholds for corn, lettuce, tomato, *B. rapa* and white pine were 320, 300, 300, 0 and 11, respectively. The latter two threshold values are well below where significant decreases occurred. The tests of significance indicate actual thresholds for these crops at between 300 and 1000 mg U/kg, the same as for the other crops.

The G soil had more organic matter and a finer texture than the B soil and, therefore, less toxicity was expected. The results confirmed this; there were no systematic decreases in germination up to 1000 mg U/kg for any of the crops. Even when the concentrations were as high as 10000 mg U/kg for the *B. rapa*, there was no significant decrease. The regression analysis did show a threshold for the *B. rapa* at 750 mg U/kg, but this was not found to be significant by the tests.

TABLE 3

Germination (%) of five crops in two soils as effected by U[1]

Crop	Control[2] (n=4)	20 (n=3)	100 (n=2)	300 (n=1)	1000 (n=1,2)[3]	3000 (n=2)	10000 (n=2)
				Uranium treatment (mg U/kg)			
		limed Boreal soil (1B)					
corn	83 TU	87	80	88	52 *		
lettuce	62 TU	45 *	--[4]	78	7 *		
tomato	33 TU	44	60	93	7 *		
B. rapa	73 TU	67	76	71	26 *	2 *	0 *
pine	59 TU	48	32 *	66	0 *		
			garden soil (G)				
corn	87	89	90	84	100		
lettuce	87	72	89	55 *	91		
tomato	68	74	65	50	94		
B. rapa	68 TU	83	81	71	67	64	21
pine	54	66	36	66	66		

[1] Only controls and those U concentrations where at least one value was significantly different from the corresponding controls are shown. Significance relative to the controls (i.e. within each row) is indicated by * and is based on one-tailed, single-degree-of-freedom contrasts with $P<0.05$.

[2] Control values followed by 'TU' are of soils where segmented regression showed a threshold U concentration; beyond the threshold, germination percentages showed a decreasing trend.

[3] There were duplicates of *B. rapa* only at 1000 mg U/kg.

[4] Planting of this treatment was inadvertently missed.

These data indicate that, at least for germination, U is not very toxic. The concentrations of As and Zn that decreased germination to 50% were about 8- and 3-fold lower than that of U for the same effect (Figure 1). Significant toxic effects of U on seed germination were not evident at concentrations below 300 mg U/kg, well above levels found in most areas contaminated by industry. In those areas where levels of 300 mg/kg are found, it is very likely that other contaminants will pose more important hazards. Arsenic and several radionuclides are often found in concert with high levels of U. Despite these findings, it is important to base final recommendations on data from crops taken to full maturity, and these results are pending.

ACKNOWLEDGEMENTS

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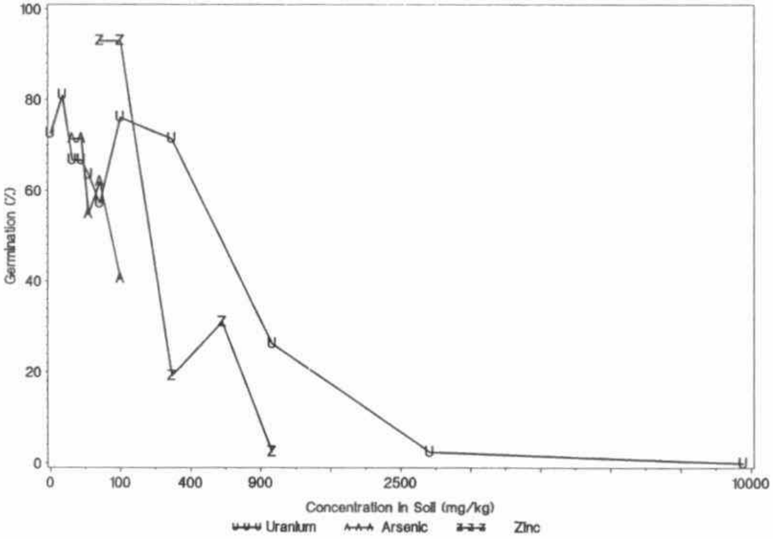
Figure 1. Germination of B. rapa as affected by uranium, arsenic and zinc in the Boreal (B) soil.



VOLUME I

SESSION A

AIR QUALITY RESEARCH

POSTER PRESENTATIONS

AP1

IDENTIFICATION OF ODOURS
THE CHALLENGE OF THE NINETIES

Andy C. Ng

and

Gary B. De Brou

Air Resources Branch
Ministry of the Environment

Toronto, Ontario M5S 1Z8

Introduction

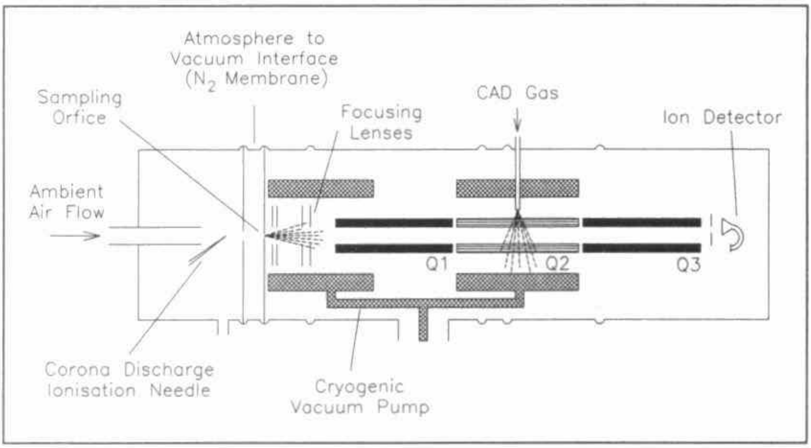
Odours, once tolerated, are now the root of many air pollution concerns. The chemical analysis of odours is one of the toughest challenges facing today's environmental scientists. Odorous compounds are generally reactive, present at trace levels, and sporadic. Consequently, techniques for odour monitoring must be capable of rapid analysis, extremely sensitive, and maintain sample integrity.

Traditional sampling, where discrete samples are collected on sorbent materials, and analysis techniques (GC/MS) are subject to chemical artifact formations, compound losses, and transformations, particularly when polar compounds are involved. An approach adopted by the Air Resources Branch is to utilize the Ministry's state-of-the-art mobile tandem mass spectrometer, TAGA 6000. Odours can be chemically characterized in a matter of minutes by advanced APCI/MS/MS techniques. "Unknown" compounds can be identified on-site through the MS/MS spectral library. The real time monitoring capabilities of the mobile TAGA 6000 provides for the determination of instantaneous levels of a variety of odorous pollutants.

The TAGA 6000 "Fingerprinting" Technique

The Trace Atmospheric Gas Analyzer (TAGA) is a tandem mass spectrometer (MS/MS) with an unique air sampling inlet system and ion source (see Figure 1). Ambient air is sampled directly at a high flow rate of 100 litres/minute into the ion source, which is operated at atmospheric pressure. Ionization of trace contaminants is achieved by chemical ionization (CI) initiated by a corona discharge. Selective ionization of chemical classes is achieved through the addition of an appropriate CI reagent to the flowing air sample. For example: atmospheric water vapour highlights ketones, aldehydes, alcohols, acids and ethers; oxygen highlights phenols, chlorophenols and acids; benzene highlights aromatic compounds and sulphurous species; and ammonia highlights amines, amides and nitrosoamines.

Figure 1: Schematic of the TAGA 6000 System.



Ionization of odorous pollutants yields a mixture of parent ions which are immediately subjected to single MS analysis by the TAGA. Pollutants are then identified by MS/MS techniques. Parent ions selected by the first quadrupole (Q1) collide with argon gas in the second quadrupole (Q2, RF only) undergoing collision activated dissociation (CAD) to form daughter ions, which are analyzed by the third quadrupole (Q3). The fragmentation pattern, or daughter ions, is characteristic of the pollutant which produced the parent ion. The resultant daughter ion spectra are then compared to a standard CAD library and the pollutants are identified. The sampling and indentification routine is achieved in a matter of minutes.

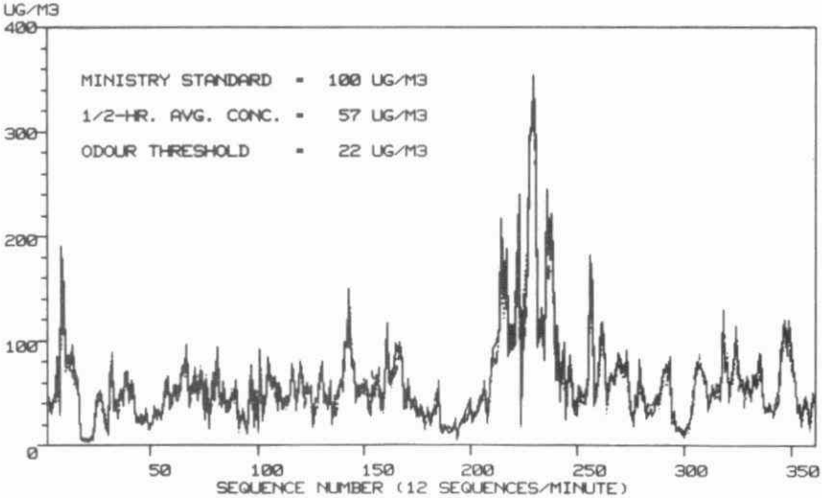
Quantitation of the Target Compounds

The target compounds are selected after determining a representative chemical fingerprint of the odours. Quantitation of a target compound is achieved by calibrating the response of the TAGA to known gas phase concentrations of the target compound. Typically, five-point calibrations are determined several times daily. Three parent/daughter ions are selected to monitor each target compound. The standard monitoring period for quantitative data is thirty minutes, with instantaneous measurements acquired every five seconds. A half-hour concentration is the average of 361 consecutive measurements. All monitoring data are correlated with meteorological information, which is recorded by the mobile TAGA unit.

Applications

The real time detection and the mobility of the TAGA 6000 allow the direct observation of short-term odour episodes (see Figure 2). For example, as shown in Figure 2, several instantaneous measurements of phenol exceeded the odour threshold limit, yet, the overall half-hour averaged concentration was below the Ministry Standard.

Figure 2: Instantaneous Phenol Levels Downwind of a Chemical Plant.



Another important capability of the Ministry's mobile TAGA 6000 is plume tracking, which is an integral part of the survey strategy. It provides unique information which is instrumental in source identification and monitoring site selection.

Summary

Over the last two years, the mobile TAGA 6000 has been applied to monitoring a broad range of volatile organic compounds, many of which have low odour thresholds; namely, acetates, amines, sulfides, phenols, PAHs, mercaptans, esters, ethers, acids, ketones, and aldehydes. Limits of detection are typically in the sub-ppb range. The ability to acquire meteorological data, in addition to the mobility of the TAGA unit, permits the tracking of source and fugitive emissions. Mobile monitoring has been effective in documenting short-term odour excursions, and fingerprinting a variety of odorous sources. The mobile TAGA technique allows real time data acquisition, providing temporal and spatial distribution of pollutants. This unit has been used to investigate the emissions from a variety of industrial sources including foundries, resin plants, incinerators, tar plants, painting operations, as well as, tire fires. Recent applications of the mobile TAGA 6000 to characterize odours will be presented.

AP2

CO_2 PRODUCTION AND CARBON CYCLING IN PRECAMBRIAN SHIELD WATERSHEDS

R. Aravena and S.L. Schiff

Waterloo Centre for Groundwater Research, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, N2L 3G1.

Concern about increasing atmospheric CO_2 concentrations have stimulated research on carbon cycling in natural systems. Northern temperate forest watersheds cover a large part of northern Ontario and Canada and have recently become the focus of intensive research regarding nutrient cycling. To understand the effect of anthropogenic influences on their carbon cycle, such as acidification and climate change, the magnitude and pathways of carbon fluxes in these ecosystems must be evaluated. Generation of alkalinity which neutralizes acidic precipitation is also a part of the natural carbon cycle in watersheds.

Our research approach involves the use of isotopic (^{13}C, ^{14}C) and chemical tools to evaluate the carbon cycling in forested watersheds in the Precambrian Shield. Isotopic fractionation during carbon transfer among the different carbon pools, makes it possible to use carbon isotopes as natural tracers to evaluate sources and sinks of carbon and transfer rates between and residence times in the various carbon pools.

The overall objective of our research is to evaluate the carbon fluxes between the main carbon pools, atmospheric and soil CO_2, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), involved in the carbon cycle of these forested watersheds. Our research is comprised of two main aspects. a) The role of soil CO2 production in carbon fluxes and the generation of acid-neutralizing capacity in a subcatchment and b) carbon mass and carbon isotope balances in the lake watershed. These whole lake mass balance will then be used to estimate ; a) The net CO_2 flux from surface water to the atmosphere and the net conversion of inorganic carbon to organic carbon in the epilimnion; b) The conversion of organic carbon to DIC and DIC input from sediments porewaters in the hypolimnion zone and; c) The importance of the DOC and POC conversion to DIC in the lake DIC budget.

The study sites, Harp and Plastic Lakes, are located in the District of Muskoka, Ontario. These two lakes with differing physical characteristic, were selected as end members by the

Dorset Research Centre of the Ontario Ministry of the Environment as part of their research concerning the effects of acidic precipitation in lake ecosystems.

The first phase of this project has focussed on the evaluation of the carbon cycle of Harp Lake. Three representative subcatchment areas (Harp 4, Harp 5 and Harp 3A) of Harp Lake watershed are being monitored to characterize the watershed inflow to Harp Lake. Plastic Lake watershed will be more intensively studied during the second phase of this project.

Soil CO_2, groundwater, streams, and lake water are being extensively sampled for isotopic and chemical analyses to evaluate spatial and temporal variations of the main carbon pools and fluxes. The main parameters that are being measured are PCO_2, temperature, pH, DIC, DOC, POC and alkalinity. ^{13}C and ^{14}C analyses are performed on soil CO_2, DIC, DOC and POC samples. Mass spectrometry and tandem accelerator mass spectrometry are being used for ^{13}C and ^{14}C analyses respectively. The lake sampling is conducted in the deepest part of the lake and includes a detailed sampling of the epilimnion and hypolimnion waters.

The main observations of the data gathered during part of 1989 and 1990 can be summarized as follow:

Soil CO_2 profiles show higher CO_2 concentration during the summer months. Root respiration, oxidation of organic matter, and diffusion of CO_2 to the atmosphere are the main processes that control the production and distribution of soil CO_2 in the soil profile. ^{14}C analyses in soil CO_2 and soil organic matter will provide us with more information about CO_2 cycling.

The average $\delta^{13}C$ value for the soil CO_2 is around -22 o/oo. The groundwaters are characterized by an average $\delta^{13}C$ value of -23 o/oo. This is a clear indication that the main process responsible for the generation of alkalinity in this subcatchment is weathering of silicates. This is important in modelling the evolution of the groundwater chemistry from recharge to discharge areas. This also implies that ^{14}C can be used as a tracer to estimate the residence time of the groundwater in the basin.

Groundwater DIC in the higher part of the basin is characterized by ^{14}C activities in the range of 116 percent carbon moderm (pmc) to 120 pmc. These values are close to the atmospheric CO_2 during 1990 recharge season. Lower ^{14}C activities (112 pmc) are observed in groundwater DIC in the discharge areas. This suggests that this groundwater was probably recharged into the aquifer at least 30 yr ago. Conversion of older DOC to DIC along the groundwater flow path could also be responsible for part of this pattern.

Stream DIC during spring time are characterized by a ^{13}C composition similar than the groundwater. However, a trend to more enriched $\delta^{13}C$ value is observed toward the end of the summer and fall. This pattern could be associated with isotopic exchange with atmospheric CO_2 and/or photosynthetic activity along the stream course. ^{14}C and PCO_2 data will provide more information to evaluate the importance of these processes.

$\delta^{13}C$ DIC profiles in the lake show a significant change in ^{13}C values from -20 o/oo to -8 o/oo in the epilimnitic waters from spring overturn to late summer. This isotopic pattern could be associated with photosynthesis and/or isotopic exchange with atmospheric CO_2. During photosynthesis, phytoplankton preferentially use the lighter carbon isotope (^{13}C) as a carbon source, leaving the residual DIC enriched in the heavy carbon isotope. Isotopic exchange with atmospheric CO_2 will change the DIC $\delta^{13}C$ signature in the same direction as photosynthesis. Since Harp Lake is in general oversaturated with respect to CO_2 and then a continuous source of CO_2 to the atmospheric CO_2 (P. Dillon, M.O.E, unpublished data), isotopic exchange should be a minor process. Preliminary ^{14}C data in lake DIC also support this statement.

The hypolimnetic DIC $\delta^{13}C$ show an opposite isotopic trend to the epilimnitic DIC. A change to more depleted $\delta^{13}C$ values from -20 o/o to almost -26 o/oo is observed toward the fall. This isotopic shift is due mainly to oxidation of organic matter falling through the water column. The average $\delta^{13}C$ for particulate organic carbon (POC) is in the order of -28 o/oo. However, the input of DIC from sediment pore water to the hypolimnion DIC cannot be ruled out. Although, preliminary measurements of DIC in surficial hypolimnetic sediment pore water, yield a $\delta^{13}C$ of -22 o/oo.

The effect of biological activity in the carbon cycling of the lake can also be observed in depth distributions of pH and DIC concentrations. pH increase in the epilimnion water from spring overturn toward the fall. The opposite is observed in the hypolimnion water. Hypolimnetic pH decreased during the same period. These patterns are the results of the redistribution of CO_2 (aq) in the water column due to photosynthesis in the epilimnion and remineralization in the hypolimnetic water and possible sediments.

DIC profiles show an opposite trend than pH profiles. For the period spring overturn to fall, they show a decreased in DIC concentration in the epilimnitic water and an increase in DIC concentration in the hypolimnetic water. The changes in DIC concentration are caused mainly by the same processes that change the pH distribution. Redistribution of CO_2 (aq) in the lake due to photosynthesis and remineralization of organic matter.

DOC cycling in groundwater, streams and lake water is being evaluated in a companion research project.

The lower DOC concentration are observed in the groundwater (~2 ppm). Higher concentration are found in the shallow part of the soil zone (LFH horizon) and in streams draining wetlands. These last areas are the major contributor of terrestrial DOC to the lake. DOC mass balances for Harp Lake indicated that this lake is net sink for DOC.

The hydrophobic fraction of DOC (humic and fulvic acids) and samples of total DOC have been processed for carbon isotope analyses.

Humics, fulvics and total DOC samples have a similar $\delta^{13}C$ range than their possible precursors, terrestrial C_3 plants and aquatic phytoplankton. ^{14}C data on DOC fractions show higher ^{14}C activities in the fulvic acid fraction compared to the humic fraction, indicating that aquatic humic substances are more refractory than the aquatic fulvic acids.

In general, surface water, including streams, wetlands and lakes contains a substantial amount of bomb ^{14}C, carbon incorporated into the global carbon cycle due to the input of ^{14}C from thermonuclear explosions after 1950. These high ^{14}C activities observed in DOC shows that cycling of a significant portion of this carbon pool in natural watersheds occurs on a short timescale (less than 40 years). This finding implies that the potential exists for anthropogenic activities, such as increase in acidic deposition, to alter the turnover rate of DOC which can have an effect in the acid-base chemistry of waters, and the mobility of metals and organic contaminants. The main results of the first phase of the research on DOC cycling in the Harp Lake watershed can be found in Schiff et al, 1990.

Preliminary sampling have also been carried out in Plastic Lake Watershed. This study site will be extensively investigated during the second phase of this project.

Schiff, S.L., Aravena, R., Trumbore, S.E and Dillon, P.J. 1990. Dissolved organic cycling in forested watersheds: A carbon isotope approach. Water Resources Research, in press.

AP3

MODELLING THE LONG RANGE TRANSPORT, TRANSFORMATION AND DEPOSITION OF MERCURY

R. BLOXAM, S. WONG, P.K. MISRA
AIR RESOURCES BRANCH
MINISTRY OF THE ENVIRONMENT

E. VOLDNER, W. SCHROEDER
ATMOSPHERIC ENVIRONMENT SERVICE
ENVIRONMENT CANADA

AND

G. PETERSEN
GKSS RESEARCH CENTRE
GERMANY

Over the last two decades information on the health effects of mercury, the buildup of methylmercury in fish in remote lakes and the role that atmospheric transport plays in the mercury cycle have increased considerably. Epidemics of methylmercury poisoning in Japan and Iran have identified the effects of methylmercury and have been used to establish dose response curves.

Although most severe mercury contamination problems due to local point sources have been eliminated, a more widespread concern about the buildup of methylmercury in predatory fish in remote lakes has developed over the past decade. In Ontario many small lakes have measured fish methylmercury values above the Ontario guideline. Indications from a number of studies suggests that the atmosphere is the primary source for the total mercury in remote lakes. Mierle (1990) examined a number of drainage basins in the Dorset, Ontario area and concluded that atmospheric loading coupled with the percentage of the drainage basin occupied by wetlands could account for observed total mercury levels in lakes. Methylation and bioaccumation processes would then play the key role in determining if these were a fish methylmercury problem for a given lake.

The most efficient means to delineate the atmospheric transport and deposition pathways is through numerical modelling. This paper presents a simplified atmospheric mercury chemistry scheme which has been implemented in an existing comprehensive Eulerian model framework (i.e. Misra et al. 1989, Venkatram et al. 1988). Some preliminary model results are discussed along with model enhancements currently being implemented.

Mercury Modelling

For this modelling effort, the mercury atmospheric system is assumed to consist primarily of 3 components: Hg°, particulate mercury and divalent mercury (i.e. $HgCl_2$ or HgO). These are the three main emitted mercury species and as indicated in Table 1 Hg° comprises > 95% of observed total mercury in the atmosphere. Of particular concern from a deposition viewpoint is the very different wet scavenging and dry deposition characteristics of these three species. Hg° is very insoluble and would thus be scavenged or dry deposited slowly (i.e. it has an estimated lifetime of several months in the atmosphere). On the other hand, HgII would be rapidly scavenged by rain and would readily dry deposit while nucleation scavenging by water droplets would efficiently remove particulate mercury. Even though observed air concentrations of HgII and particulate mercury are small they could form a significant fraction of the wet scavenged mercury and thus affect deposition patterns.

The modelling approach was to put a three species mercury system into an existing Eulerian model framework (i.e. Acid Deposition and Oxidant Model) using the best currently available emission inventory for eastern North America along with information on dry deposition rates, boundary conditions, and aqueous chemistry. The Eulerian model is modularized with sections dealing with transport and diffusion, dry deposition, mixing by clouds, scavenging within clouds followed by aqueous chemistry and wet deposition, and gas phase chemistry. The model domain encompasses eastern North America using a 33 x 33 grid with each cell 127 km by 127 km. The model includes 12 vertical layer distributed logarithmically to the 10 km level. Meteorological fields needed to run this model (i.e. winds, temperatures, stabilities, clouds, precipitation etc.) are derived in a preprocessing operation and put into the model as inputs. The other inputs needed are geophysical data such as terrain height and land use categories (percentage of grid: water, forest etc.) and emission rates for each grid square (or for individual point sources).

(a) Mercury Emissions

The anthropogenic emission inventory for mercury is dated and requires updating. Estimated total anthropogenic emissions are ~ 650 tonnes from the U.S. and ~ 31 tonnes from Canada. For the U.S. the important source categories were fossil fuel combustion at over 20%, use of paint and electrical equipment at 55%, non-ferrous metal smelters at ~10% and sewage sludge and municipal waste incineration at ~ 15%. The breakdown of Canadian emission was base metal recovery 45%, fuel combustion ~ 25% and paint volatilization ~ 15%. Preliminary model runs were performed by griding these emissions from state and province total emissions. In particular, the consumer goods part of the emissions was assumed to be related to population centres. In detail the distribution of these emission could be very different from that used. The use of mercury in paints as a fungicide agent would not necessarily be the same in different states.

Speciation of the emissions for initial model runs simply used a 90:5:5 ratio for Hg°: HgII : particulate mercury. A better breakdown of the emitted species is being prepared using sector speciation percentages suggested in Europe. For the North America emissions this leads to a 81:17:2 ratio for the mercury species.

Natural emissions of Hg° from soils or vegetation are poorly known. Model runs made use of emission factors over land which were a function of temperature (zero emissions below 0°C). Emissions from water surfaces were assumed to be zero. Over the eastern North America area, modelled natural emissions were similar in total to anthropogenic emissions. Although data is very limited a revised natural emission inventory is being produced.

(b) Gas phase mercury chemistry is poorly known at present. Given the low observed values of air HgII and particulate mercury concentrations, model runs have been performed assuming no net gas phase chemistry. This means that reduction reactions are assumed to nearly balance oxidation reactions. This assumption would affect the relative air concentration of the mercury species and therefore alter deposition patterns.

For aqueous phase chemistry the only reaction directly modelled is oxidation of Hg° by O_3 to give HgO. This reaction then allows more of the very insoluable Hg° to be adsorbed into water droplets. This mechanism was used in initial model runs.

More recent information suggests that other aqueous phase processes such as reduction by sulphate and adsorption of HgII or Hg° to particles in water also occur. Observations indicate that most of the mercury in precipitation ends up adsorbed on particles and that assumption will be used in future model runs.

(c) Dry deposition rates of Hg° should be small since the substance is very insoluble. Model runs to date have used a zero dry deposition velocity, however, more recent data suggests a small deposition to forests in the summer (i.e. ~ 0.03 cm s^{-1}) with little deposition to other surfaces or at other times. Further model runs will incorporate dry deposition of Hg° to forests. Even though the deposition rate is small the fact that air concentrations of Hg° comprise ~ 95% of the total mercury in air can result in significant dry deposition.

On the other hand, HgII species dry deposit very rapidly while particulate mercury is assumed to dry deposit at a rate similar to that for sulphate.

(d) The last important consideration for modelling the mercury system is the domain boundary values of the mercury species. Since Hg° molecules have a long lifetime in the atmosphere, boundary values of 1.5 ng m^{-3} at ground level are observed in remote areas. Particulate mercury concentrations of ~ 0.02 ng m^{-3} are also observed away from source regions. Model runs will make use of well mixed profiles for these compounds at all domain boundaries.

Model Results

Initial model runs were intended to provide only a magnitude comparison of modelled air and precipitation mercury concentrations with the very limited observed data (discontinuous air and precipitation readings at a few sites in North America). The model was run for a five day period in April 1981 for which meteorological data was already available. The last two days of these model runs produced the following results.

(1) Air concentration of Hg° were in the 1 to 3 ng m^{-3} range which is similar to the average observed values of 1½ to 4 ng m^{-3} away from source areas.

(2) Modelled air concentrations of HgII and particulate mercury were less than 0.05 ng m^{-3} using 5% of total emissions for each of these species. Very few reliable observations exist. Measured average particulate values in the New England area were ~ 0.06 ng m^{-3} while values in Wisconsin averaged ~ 0.02 ng m^{-3}.

(3) Concentrations of HgII and particulate mercury in precipitation varied strongly with precipitation amount which is consistent with rapidly scavenged species. For moderate precipitation areas both HgII and particulate mercury concentrations in precipitation were in the ½ to 4 ng l^{-1} range.

On the other hand, scavenging of Hg° produced only about 1 ng l^{-1} of mercury in precipitation.

The total modelled values of 3 to 7 ng l^{-1} is moderate precipitation is lower than the observed values of 10 to 20 ng l^{-1} but it must be kept in mind that the speciation of the emissions was very crude.

Future Work Plan

All aspects of the model formulations and the emission inventory are being updated as discussed above. Once this has been completed a series of sensitivity tests will be performed. Sensitivity test will be performed for some of the areas in which input data and model parameters are most uncertain. The sensitivity runs will be done for episodes of 5 to 10 days with the first 2 or 3 days used for model warm up.

1. Base Case Run.
2. 50% increase in anthropogenic emissions.
3. 100% increase in natural emissions.

4. Reduce anthropogenic HgII emissions and increase anthropogenic particulate emissions
   (a) 81% Hg°, 12% HGII, 7% particulate
   (b) 90% Hg°, 8% HGII, 2% particulate.

5. Dry deposition of Hg°:
   (a) Reduce the surface resistances to forests by a factor of 2 (i.e. deposition velocities closer to Lindbergs data).
   (b) Use surface resistances for cultivated levels etc. as twice the values for forests.

6. Final products of aqueous oxidation:
   Use 80% particulate mercury and 20% HgII as the species put into air when droplets evaporate.

7. Boundary conditions:
   (a) Reduce boundary values of Hg° by a factor of 2.
   (b) Reduce boundary values of particulate mercury by a factor of 2.

The University of Toronto has recently undertaken a 3 year project to model the cycling and bioaccumulation of mercury in remote Ontario lakes. To drive this modelling effort the loading of mercury deposited from the atmosphere is needed. As an adjunct to our current atmospheric modelling project long term gridded wet deposition of mercury will be produced using a simpler parameterization of the mercury system in a Lagrangian model. This will serve as a preliminary wet deposition field until the more detailed evaluation of the Eulerian mercury model has been completed. At that time an updated deposition field will be produced which reflects the knowledge gained in this project.

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Venkatram A., Karmachandani P.K., and Misra P.K. (1988). Testing a Comprehensive Acid Deposition Model. Atmospheric Environment 22, 737-747.

Table 1 Typical continental background air concentrations of important atmospheric mercury forms and their respective Henry's law constants.

Compound	Concentration ng m^{-3}	Henry's law constant $H=[HgX]_g/[HgX]_{aq}$ (dimensionless)
Hg^0	2 - 4	0.3
$(CH_3)_2Hg$	0 - 0.01	0.3
CH_3HgCl	0 - 0.1	1.5×10^{-5}
$HgCl_2$	0 - 0.1	10^{-8}
particulate Hg	0 - 0.1	

AP4

ABSTRACT

An Investigation of Vibration Isolation in a House for Reduction of Train Vibration

Part 2: Characterization of Ground Vibrations from Trains

and

Part 3: Effectiveness of an Isolation System in Reducing Train-Induced Ground Vibrations

1. Background

The increased use of land beside railway lines for residential housing during the past decade has produced a rise in the number of complaints from nearby residents on the level of vibrations within their homes. These complaints have lead to a search for ways to isolate new homes from the effects of train-induced vibrations.

One method that appears promising is to place elastomeric pads between the ground and the superstructure. The method has been used successfully for many decades to isolate buildings from subway-induced ground vibrations and is now being recommended for residential structures near railway lines. However, the applicability of this method for different types of residential structures has not been tested nor has its effectiveness in reducing structural response to train-induced ground vibrations been demonstrated. Both aspects should be extensively examined from technical and financial viewpoints before elastomeric pads can be widely accepted as a satisfactory procedure for isolating residential construction. The goal of this three-part investigation was to provide some of this valuable information.

Part 1 of the investigation (Evaluation of Transducer Mounting in the Ground) was presented at the 1989 Technical Transfer Conference. Parts 2 and 3 are being presented at this year's conference. Part 2 (Characterization of Ground Vibrations from Trains) studied the frequency and propagation characteristics of train-induced ground vibrations at three sites in Southern Ontario. Part 3 investigated the effectiveness of an elastomeric pad system incorporated into a recently constructed two-storey row house. The residential structure was built within 50 m of a double-track rail line at one of the sites studied in Part 2.

2. Part 2 (Characterization of Ground Vibrations from Trains)

Frequency characteristics of ground-induced train vibrations were investigated at three sites located within the Ottawa-Montreal-Toronto triangle. The sites had substantially different surface profiles and soil conditions (soil type and depth). Track geometries at two of three sites were similar (track elevation at same level as adjoining land) as were track constructions (continuously welded rails supported on wood ties) and track number (double-track line). Rail traffic at each site contained both freight and passenger trains.

Ground vibrations were measured simultaneously at five stations along a measurement line perpendicular to the tracks with station distances ranging from 11 m (Station 1) to 160 m (Station 5) from the centreline of the tracks. Triaxial accelerations - vertical, transverse (perpendicular to the tracks) and longitudinal (parallel to the tracks) - were measured at Stations 1, 3 and 5 and vertical and transverse at Stations 2 and 4. Accelerometers were attached to the ground using the wooden mounting plate (175x175x19 mm) studied in Part 1 of the investigation.

One-third octave band analysis of vibrations produced by passenger and freight trains showed that site conditions were the most important factor affecting the frequency content and amplitudes of ground vibrations. Attenuation rates of one-third octave frequencies within the dominant frequency range were also site dependent. Although there was some indication of dependence of peak and broadband acceleration amplitudes on speed, type of train and train weight, the influence of site conditions greatly overshadowed any of these other variables.

The combination of a simplified site-dependent frequency spectrum near the track and a corresponding site-dependent attenuation rate is suggested as a design basis for vibration isolation systems of houses near railway tracks.

3. Part 3 (Effectiveness of an Isolation System in Reducing Train-Induced House Vibrations)

Part 3 examined the effectiveness of an elastomeric pad system in reducing the transmission of train-induced vibrations into a residential structure. The isolation system was placed between the superstructure and the top of the basement foundation walls in a two-storey residential row house. The house, a conventional wood-frame structure with a special precast concrete panel first-floor system, was within 50 m of a double-track railway line. The line was heavily used by commuter GO trains throughout the day. About 12 passenger trains and six freight trains also used the line on a daily basis.

House response to train passages was measured at four stations using accelerometers. Two stations were on the first floor slab and two directly below in the basement near the top of the concrete foundation wall. The accelerometers at each station on the first floor were paired by direction with the accelerometers in the basement. The pairing of station accelerometers was essential for the evaluation of the elastomeric pad system.

The measurements, taken before the installation of partition drywall, showed that

1) train-induced vibrations in the section of the house closest to the tracks were, over certain frequency ranges, smaller in the superstructure than in the foundation wall.

   The magnitude and frequency range of the reduction varied with direction; 3 to 9 dB from 40-80 Hz in the vertical direction, 4 to 10 dB from 50-125 Hz in the transverse direction (perpendicular to the track) and 4 to 16 dB from 25-125 Hz in the longitudinal direction. Outside these frequency ranges, vibrations in the superstructure were up to 10 dB larger than those on the foundation wall.

2) vertical vibrations in the section of the house farthest from the tracks generally exceeded those in the foundation wall throughout the 6-125 Hz frequency range.

   A possible reason for this behaviour was undetected material short-circuiting of the isolation system combined with low levels of train-induced vibrations in both the house and the ground at this location.

Because of the uncertainty in the effectiveness of this isolation system, additional studies of elastomeric pad systems should be undertaken.

AP5

SIMULTANEOUS REAL TIME DETECTION OF MERCURY AND HYDROGEN CHLORIDE IN AMBIENT AIR

M.D. Corbridge*, G.B. De Brou, A. Ng and N.S. Karellas
Air Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario

Introduction

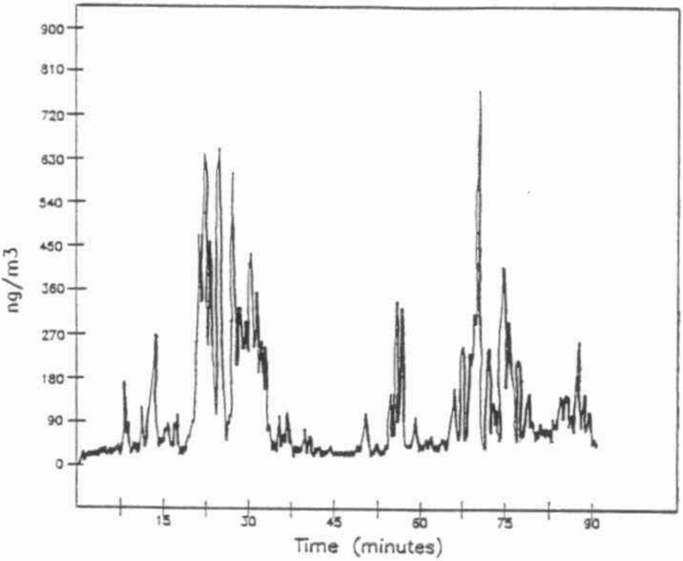
An incinerator plume may be located by simultaneously measuring, in real time, two of the plume constituents, namely mercury and HCl. A coincident elevation in ambient levels of both targeted pollutants can provide evidence that the pollutants originate from the same source. Chemical characterization of plumes via stationary monitoring devices is difficult given the capricious nature of local meteorology; however, by placing the monitoring devices in a mobile laboratory, the incinerator plume can be effectively tracked.

In this study, techniques were developed to concurrently measure trace levels of gaseous HCl and elemental mercury vapour in ambient air. HCl was measured using an atmospheric pressure chemical ionization (APCI) tandem mass spectrometer (TAGA 6000) while mercury was detected by a spectrophotometric method.

Mercury Analysis

Elemental mercury was monitored by a modified Scientrex HGP-2 mercury monitor because of its high sensitivity and real time response. Spectrophotometric analysis of mercury vapour was achieved by Zeeman absorption of the 254 nm mercury resonance line. Extensive work was performed prior to the survey to determine the detection limits and establish an appropriate QA/QC procedure. Detection limits were determined based on background measurements and were in the range of 10-15 ng/m^3 (2 ppt). Five-point calibrations, over a range of 0 - 500 ng/m^3, were performed to determine the linearity and consistency of instrument response. The data showed that it remained constant to within 5% over a period of 12 hours. Figure 1 is an example of some real time data for elemental mercury recorded by the Scintrex HGP-2 analyzer in an urban environment.

Figure 1: Real Time Data of Elemental Mercury.



Hydrogen Chloride Analysis

Since commercial HCl detectors lack the sensitivity for low ppb detection, a method was developed to monitor gaseous HCl via APCI/MS/MS. The ion chemistry under APCI conditions is dominated by dissociative attachment reactions:

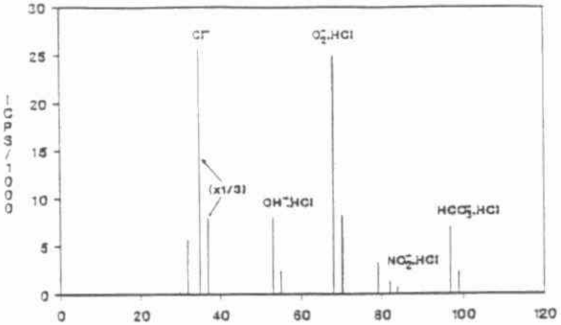
$$Y^- + HCl \rightarrow YH + Cl^-$$

where Y refers to OH, SO_2 or CO_3, and by reactions leading to the formation of adduct ions:

$$XY^- + HCl \rightarrow XY^- \cdot HCl$$

Where XY may be OH, O_2, NO_2 or HCO_3. A background-subtracted mass spectrum of HCl obtained by admitting trace amounts of HCl gas to the APCI source is shown in Figure 2. The anions at masses (M-1), (M+17), (M+32), (M+46) and (M+61) amu are produced by HCl deprotonation, and HCl clustering with OH^-, O_2^-, NO_2^- and HCO_3^-.

Figure 2: Single MS Spectrum of HCl



Since Cl⁻ ion may arise from a variety of Cl-containing compounds it is not a good identifier of HCl in the presence of other chlorinated species. It was found however, that selective monitoring of the cluster ion $O_2^- \cdot HCl$, and to a lesser extent $OH^- \cdot HCl$, together with the ability of MS/MS to separate the ^{35}Cl and ^{37}Cl isotopes, provides a reliable mechanism for identifying HCl in a complex matrix including other chlorinated compounds. The MS/MS daughter ion spectra of the cluster ion $O_2^- \cdot H^{35}Cl$ and $O_2^- \cdot H^{37}Cl$ is shown in Figure 3A and 3B. Note that the hydrated ion of O_2^- at 50 amu, shown in Figure 3A, is a daughter ion of double-hydrated ion of O_2^- at 68 amu. The limit of detection for HCl was approximately 0.5 μg/m³ (70 ppt). The linear detection range, determined by calibration, was 0 to approximately 60 μg/m³.

Figure 3A: Daughter Ion Spectrum of $O_2^- \cdot H^{35}Cl$

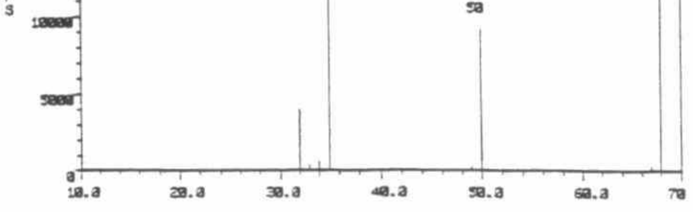
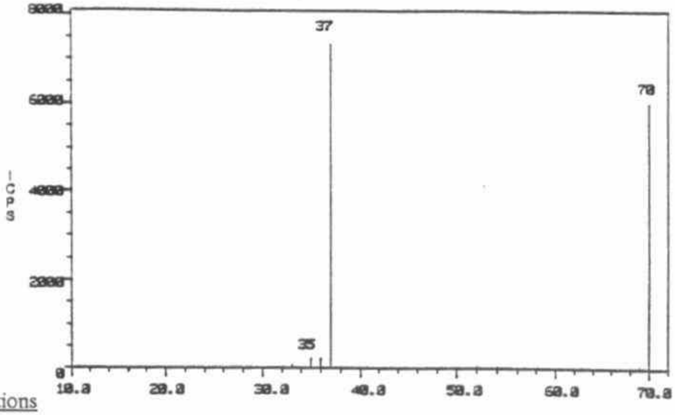


Figure 3B: Daughter Ion Spectrum of $O_2^{-} \cdot H^{37}Cl$



Applications

The determination of real time levels of elemental mercury and gaseous hydrogen chloride, in conjunction with a mobile TAGA unit, may provide unique information regarding the impact of incinerator emissions at the ground level. Potential sources of mercury and HCl include municipal waste and biomedical waste incinerators. This technique, which has been recently field tested, will be applied to ambient air studies in the future, where the simultaneous emission of HCl and Hg occurs.

AP6

A Residence Time Analysis of Air Data from the Acidic Precipitation in Ontario Study (APIOS)

N. W. Reid, A. Tang, M. A. Lusis and D. Yap
Air Resources Branch
Ontario Ministry of the Environment,
Toronto, Canada

Introduction

Acid rain monitoring has been carried out by the Ontario Ministry of the Environment since 1980 under the auspices of the Acidic Precipitation in Ontario Study (APIOS). One of the objectives of the study has been to determine the major emission areas contributing to deposition of acidifying species to sensitive regions of the province.

Previous analyses combined meteorological and deposition data to characterise the contributions of the Sudbury smelters and the long range transported component to deposition in Ontario (e.g., Chan et al., 1982; Tang et al., 1986). The present analysis also uses the directional information contained in air parcel back trajectories, but goes further to extract information on distance to define the relevant source areas more precisely.

Experimental

The concentration data used in this study were obtained at Dorset, in the acid-sensitive Muskoka region of central Ontario. The main thrust of this work was aimed at concentrations in air, which were determined using a filter pack, with a 24 hour sampling period. Sulphate and nitrate were collected on a teflon filter, sulphur dioxide on a pair of cellulose filters impregnated with potassium carbonate in glycerol. In addition, some analyses were carried out on concentrations of sulphate and nitrate in precipitation. Precipitation samples were collected in a wet-only sampler (Aerochem-Metrics), also with a 24 hour sampling period. All samples were analysed by ion chromatography, after appropriate work up (Chan et al., 1985).

Residence Time Analysis Procedure

The residence time analysis procedure has been described by Poirot and Wishinski (1986). Briefly, air parcel back trajectories were calculated for each day for which a valid sample datum was obtained. The data, and the associated back trajectories, were then classified as high or low, by comparing the concentration with predetermined levels. These levels were chosen to be approximately equal to the 25th and 75th percentiles of the concentration of that species.

Eastern North America was overlaid with a 127 by 127 km grid, and each back trajectory was disaggregated so as to count the trajectory length falling within each grid square. This corresponds directly to the amount of time that the air parcel spent over the grid square. A geometrical correction was then applied to account for the fact that trajectories are more likely to pass over grid squares close to the receptor, and, in the limit, all pass over the home grid square.

The result of this analysis is an estimate of the relative amount of time spent over each grid square by air parcels corresponding to the observation of high or low concentrations at Dorset.

A sample of the results is given in Figure 1, which shows the residence time for air parcels associated with the observation of high concentrations of sulphate in air at Dorset. The contours contain respectively the areas within which the trajectories spent 25, 50 and 75% of their travel time for the specified conditions.

Results and Discussion

Air Concentrations

The main emphasis in this study was to apply residence time analysis to air concentrations of particulate sulphate and nitrate and gaseous sulphur dioxide. The analysis was confined to those days on which precipitation did not occur, since this reduced the perturbing effects of fronts and strong convective activity on the calculated back trajectories. The analysis was applied to a data set covering the years 1980 to 1985 inclusive, and was broken down by seasons.

The patterns for all three pollutants are similar. For high concentrations the trajectories spend most of their time to the southwest of Dorset, for low concentrations the isopleths lie in northern Ontario, and over Hudson Bay. The trajectories appear to be relatively short in the summer time, so that the 25% isopleth for high concentrations lies in southern Ontario and northern Ohio. In the winter this isopleth stretches much further to the south, and encompasses the Ohio Valley for sulphate and nitrate. The 75% isopleth is very similar for both seasons. For SO_2 the isopleths cover a smaller area than for sulphate or nitrate, particularly in the summer. This is consistent with the photochemical conversion of SO_2 to sulphate, which occurs more rapidly in the summer than in the winter.

Precipitation Concentrations

Although the calculated back trajectories are expected to be less accurate under precipitating conditions, the residence time analysis was also applied to high and low concentration categories of sulphate and nitrate in precipitation. These analyses were performed for all data, without a seasonal breakdown, and a sample is shown in Figure 2, which corresponds to the case of high sulphate concentrations. Again the difference between the patterns for high and low concentrations is very clear (high concentrations are associated with source areas to the south), while the behaviour for sulphate and nitrate is similar. These patterns indicate a significant westerly component, which is absent in the patterns for the air concentrations.

Overall

The residence time analysis very clearly implicates sources to the south, particularly including locations on the Ohio River Valley, as being associated with the observation of high concentrations of pollutants at Dorset. This observation applies to both air and precipitation concentrations. Conversely, low concentrations are associated with air parcels from the north. These results are consistent with a number of earlier analyses. The present analysis is unique in its ability to delineate the boundaries of the implied source areas.

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Figure 1. High sulphate, summer

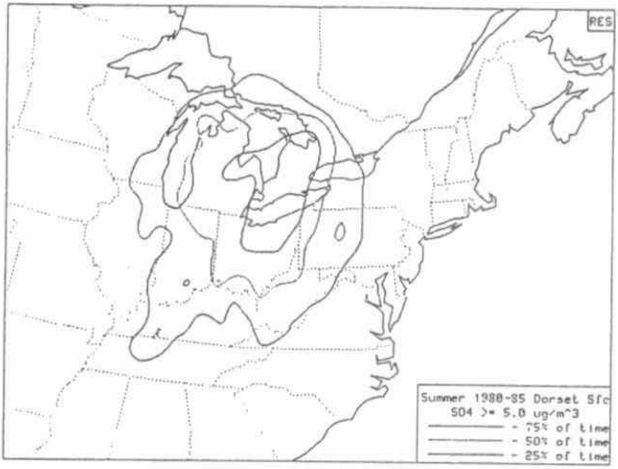
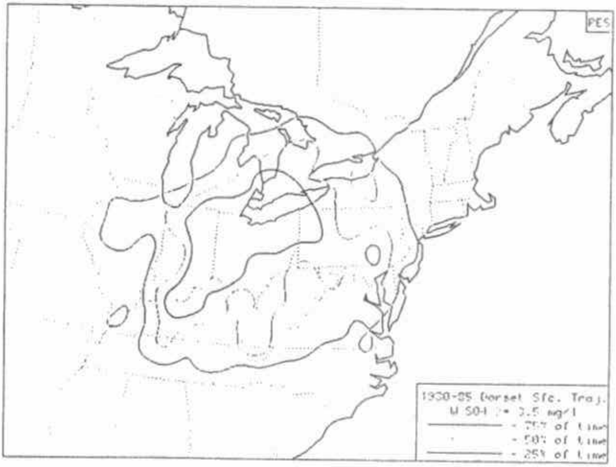


Figure 2. High sulphate in precipitation



AP7

MICROWAVE INDUCED CATALYTIC DECOMPOSITION OF SOME GASEOUS AIR POLLUTANTS

M. C. Depew, T. Dineson, M. Y. Tse and J. K. S. Wan,
Department of Chemistry, Queen's University,
Kingston, Ontario, K7L 3N6

INTRODUCTION

The deleterious effects on all living things of a variety of pollutants ubiquitous in the air, water and soil environments especially in industrialized countries have been recognized and extensively studied for several decades. Technologies for the reduction of additional sources of pollution as well as those directed at reversing or cleaning-up existing problems are the focus of much interest both academically and economically. In the areas of air pollution some of the principal concerns have been the effects of the acid gas pollutants SO_2 and NO_x, and the increasing changes effected by the vast volumes of CH_4 and CO_2 on the global weather patterns; the damage to the protective atmospheric ozone layer by hydrocarbon and halohydrocarbon effluents, and the carcinogenic and mutageic potentials of polyaromatic hydrocarbons and halogenated hydrocarbons.

This project involves the development and application of a novel technology which utilizes the selectivity and efficiency of mirowave interaction with different materials in order to facilitate the catalytic destruction of several airborne pollutants. The process has been named microwave induced catalysis and has been applied successfully to initiate and control a variety of chemical reactions of industrial significance including the conversion of methane to ethylene (1), the dehydrogenation of alkanes (2), and the oxidation of hydrocarbons using water (3).

The concept stems from the fact that different materials have an extremely wide range of abilities to absorb microwave radiation. Thus, most organic and many inorganic materials are poor absorbers of microwave and behave as though essentially transparent to incident microwave radiation. Other strongly absorbing materials such as many paramagnetic or ferromagnetic metals can concentrate and efficiently convert microwave radiation to heat. The catalytic technology utilizes this selectivity; the catalyst material consists of or contains the strongly absorbing "sensitizer" and is also chosen for its ability to facilitate the desired reaction, while the bulk of the reaction medium remains at ambient temperature and reactions occur primarily at the catalyst surface. Another particular advantage to microwave radiation as the reaction energy source is the ease with which it can be gated or pulsed. Appropriate pulse durations and periods allow control of reaction selectivity though control of the temperature of the catalyst surface; this also facilitates desorption of products from the surface and minimizes back reactions.

The general concept of microwave induced catalysis is applicable to a wide variety of reactions and the relative simplicity of the experimental design should allow modification to suit many industrial applications of environmental benefit. Indeed this concept has been described as an "enabling technology" whose applications have much wider significance than can be presented here. This report will briefly describe the application of this technology to the destruction of SO_2 and NO_x by reduction rather than conventional oxidative methods, and the dehalogenation of both aromatic and aliphatic hydrocarbons. Other applications to conversion of methane and CO_2 are also under consideration.

EXPERIMENTAL

The experimental methods and procedures for microwave catalysis reactions are a continually evolving process and there is no one general apparatus suitable for all applications; rather the optimal apparatus depends on the chemical system to be investigated. Early experiments to test the viability of the technique were illustrated using a simple commercial microwave oven modified to contain a pyrex reactor and connected to a vacuum line for injection of gaseous reagents; direct GC or GC/mass spectrometric detection is readily incorporated (Figure 1a). Subsequently a 3 kW variable Cober magnetron was used as the power source with appropriate microwave and electronic hardware to allow monitoring of the power absorbed or reflected by the reactor (Figure 1b). This design using millisecond pulses of kW power produced significantly improved conversions with much greater product selectivity compared to the microwave oven set-up in which powers of 250-400 W were produced and pulse durations of 2 - 10 s were typical. Further details of the experimental parameters are discussed elsewhere (4,5). Typically in experiments with either the acid gases or the halogenated compounds the reagents were flowed into the catalyst bed diluted in an inert gas and in concentrations ranging from 5 - 50 % until the catalyst bed was saturated. Microwave irradiation was then initiated while further reagent flow was continued. GC analysis was done on a Hewlett-Packard (Model 5890A) GC with either TCD or FI detection as appropriate. Commercially available supported catalysts including Ni-1404, Ni-1600, Cu-1700, Cu-1132, Ti-0404 from Harshaw/Filtrol Partnership, C-12 CO conversion catalysts from Chemetron-Girdler, C101-V_2O_5 from Catalyst and Chemicals, and Ni, Fe, Cu, graphite and CuO powders were used as well as some in-house catalyst pellets. For certain of the experiments initial activation of the catalyst under H_2 (30 kPa) while irradiating with ten 5 s pulses of 400 W average microwave power was performed.

RESULTS AND DISCUSSION

SO_2 and NO

Our aim in experiments with either of these acid gas reagents was to effect reduction of the starting material with the resulting production of O_2 and either S or N_2. In both cases it was possible to remove >99 % of the acid gas reagent with the corresponding production of O_2 as shown in (Figures 2,3), although in the SO_2 experiments only the total S produced was measured and the S containing product has not yet been speciated; it is however, adsorbed on the catalyst. Further experiments to elucidate aspects of the reaction mechanism using ethylene as a scavenger are underway.

In experiments with NO at long reaction times some N_2O was produced as well as N_2 and O_2. The appearance of this product indicated the oxidation of the catalyst surface; this could be dramatically hindered (i.e. irradiation time before catalyst oxidation increased by more than an order of magnitude) by mixing a coreductant (~10 % by volume) such as CH_4, H_2, or CO in the reagent gas stream.

Regeneration of the catalysts used by microwave irradiation under H_2 allowing repeated reuse of the catalyst material was readily accomplished.

Dehalogenation of Aliphatic and Aromatic Hydrocarbons

Halogenated and polyhalogenated compounds which are of environmental concern exhibit a variety of different structural features; a few model systems have been studied to demonstrate the potential of microwave induced decomposition towards these pollutants. These include methyl chloride, methyl bromide, dichloromethane, several chlorobenzenes, and triphenylmethyl chloride and bromide. In each case the catalyst bed was presaturated with the reagent of interest (15 -50 % in He) and the gas phase recirculated over the catalyst bed for the duration of the reaction. In each system the halogenated reagent was decomposed: for methyl chloride the only products detected were methane and dimethyl ether, whereas methyl bromide irradiation resulted in the formation of methane, methanol and dimethyl ether. Results for the dichloromethane and chlorobenzene decompositions are shown in Figures 4 and 5. In all cases substantial concentrations of chlorine were detected by elemental analysis of the catalyst material. As can be seen in Figure 4 dichloromethane dehalogenation appears to occur in a stepwise fashion with methyl chloride being formed as a reaction intermediate. Chlorobenzene was slightly more difficult to remove completely; 3.9 s microwave pulses reduced its concentration by ~60% with formation of benzene, CO_2, water and methane, while longer pulse durations effectively completely removed the starting material and also decomposed the benzene product to the less toxic products water, CO_2 and methane. Mechanisms for such surface catalysed reactions are very difficult to prove, however, the stepwise dechlorination of dichloromethane and the products formed in all the systems are consistent with free radical mechanisms. Furthermore, the microwave induced dehalogenation of either triphenylmethyl chloride or bromide over Fe or Ni powder in benzene produced a solution exhibiting the Electron Spin Resonance spectrum of the stable triphenylmethyl radical.

CONCLUSION

Microwave induced catalysis is a very versatile, fast, and energy efficient process which through suitable catalyst selection can readily be applied to the destruction or removal of substantial concentrations of gaseous or liquid pollutants. The microwave hardware components are commercially available and can be modified for a variety of applications. Ongoing experiments using this technology are directed at conversion of CO_2 to carbon and O_2, and methane conversions as well as the design and assessment of a higher power, shorter duration (megawatt / microsecond) microwave reactor for the processing.

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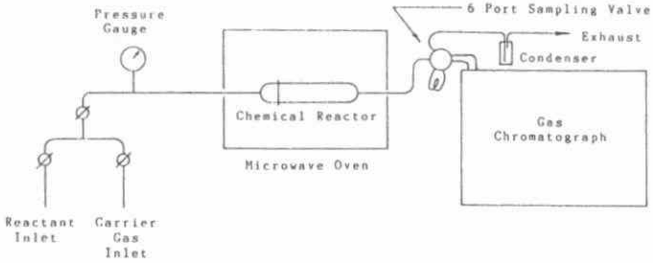

Figure 1a A Schematic Diagram of the Flow-Through Microwave Oven Reactor.

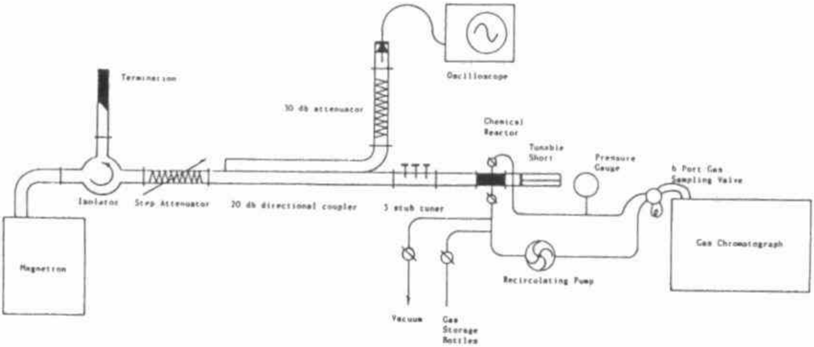

Figure 1b A Schemcatic Diagram of the Microwave Waveguide Reactor System: The Recirculating Flow Reactor

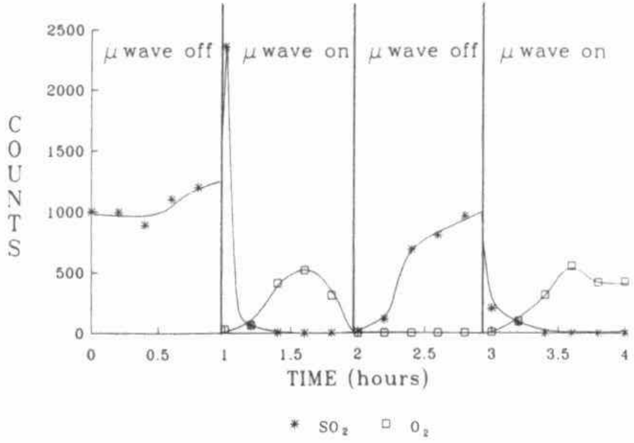

Figure 2 Decomposition of SO_2 Over Nickel/Nickel Oxide Catalyst (Harshaw Ni-1404)

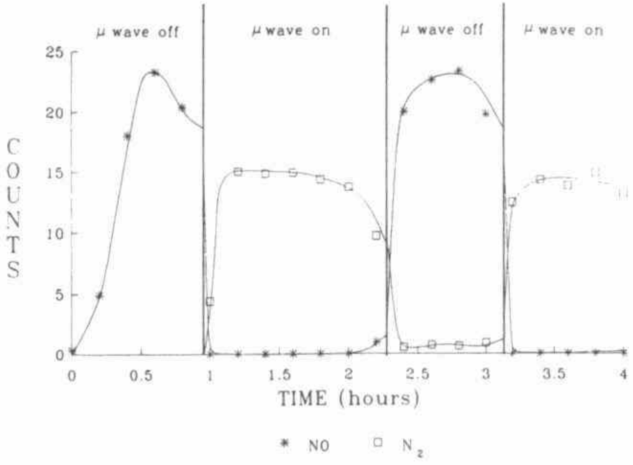

Figure 3 Decomposition of NO Over Iron Oxide Catalyst (Girdler C-12)

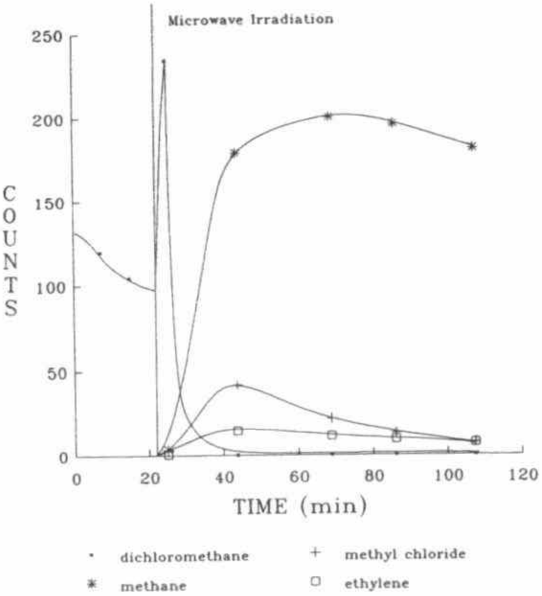

Figure 4. Decomposition of Dichloromethane in the Recirculating Microwave Oven Reactor

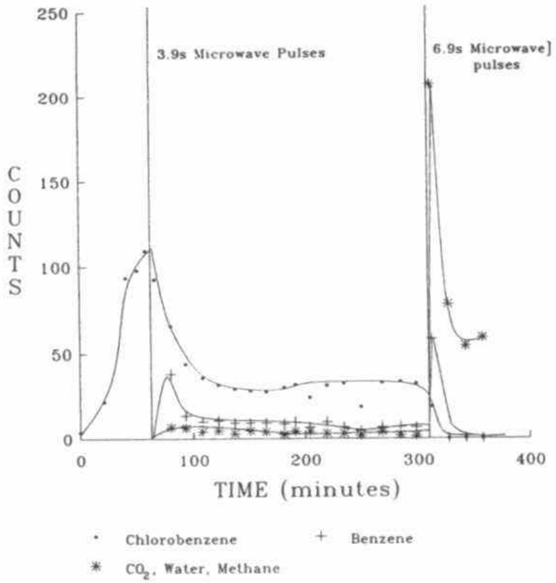

Figure 5 Decomposition of Chlorobenzene Over Nickel/Nickel Oxide Catalyst (Harshaw Ni-1404)

AP8

MESOSCALE AND LONG RANGE TRANSPORT MODELS ARE COMBINED TO MODEL POLLUTANTS ORIGINATING FROM LOCAL AND DISTANT SOURCES.

M. Niewiadomski, The MEP Company, Markham, Ontario, L3R 9T2

1. INTRODUCTION

A mesoscale meteorological model 'GESIMA' is combined in this study with the Acid Deposition and Oxidant Model, ADOM. The two models will form a nested grid model allowing simulations of transport, chemical transformations and deposition of atmospheric pollutants with horizontal resolution of 20 km, as compared with the 127 km resolution of ADOM alone. Such a model can then be used to evaluate the impacts of various abatement strategies of the emissions of the precursors, nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in urban areas of Southern Ontario, for the control of ozone and other oxidants, or the impacts of variable controls of SO_2 and NO_x emissions for the control of acid deposition.

The ADOM model does not generate its own meteorological fields, using instead the 3-D fields of wind, temperature, humidity, and other meteorological parameters produced by a large scale NWP model of the Canadian Meteorological Centre (CMC). The high resolution simulations with ADOM are made possible by replacing those fields with 3-D meteorological fields generated by the mesoscale model.

The full run of the combined, nested model will consist of:

a. The 'regular', large scale run of ADOM using the meteorological fields taken from the output of the CMC model.

b. The high resolution run of GESIMA in the area of particular interest. The initial and boundary conditions will be derived from the CMC output.

c. The high resolution run of ADOM using the 3-D meteorological fields generated in step b. and the initial and boundary conditions derived from the results of the step a.

In this project the simulations are planned for two areas of Southern Ontario. Each domain will consist of 9 cells of the 127 km CMC grid of ADOM, with the Toronto cell in the centre of the first domain and the Windsor cell in the second one. In future, the area of simulations could be extended to the entire high ozone corridor extending from Windsor to Quebec City.

Two periods for which detailed air quality and emission data are available will be simulated, namely April 21 - 24, 1981 (the OSCAR IV period) and a high ozone episode of August 2 - 5, 1988. The results of the nested grid model will be compared with those of the 'regular' ADOM and with the observational data. The simulation will be carried out on the CRAY X-MP computer of the Ontario Centre for Large Scale Computation.

The project started in July 1990. The tasks completed to date (September 1990) concerned mostly modifications of GESIMA to allow its coupling with ADOM and assembling the data necessary for its run. The following sections describe those data, provide some background information and describe the recent modifications of GESIMA.

2. BACKGROUND

2.1 ADOM

The ADOM (Acid Deposition and Oxidant Model, sometimes also referred to as 'TADAP') is a comprehensive, sophisticated Eulerian model simulating the regional scale transport, chemistry and both 'wet' and 'dry' deposition of various atmospheric pollutants. The model has been developed by the ERT and MEP companies under the sponsorship of the Ontario Ministry of the Environment, Environment Canada, Umweltbundesamt (Germany), and Electrical Power Research Institute (USA). For details see Venkatram et al. (1988).

For the Canadian applications, the model is usually run using the '127 km' CMC grid (which actual size in the Toronto area is about 115 km) and the 3-D meteorological fields generated by the CMC NWP model. The model has 12 vertical layers, extending to 10 km and ranging in thickness from 56 m at the ground to about 2500m at the upper boundary.

2.2 GESIMA

GESIMA (GEesthacht SImulation Model of the Atmosphere) is a sophisticated, mesoscale model developed at the GKSS Forschungszentrum in Geesthacht, Germany. The model solves the non-hydrostatic, anelastic equations of motion in terrain-following coordinates using a predictor-corrector scheme. The dynamic pressure is computed using a conjugated gradients method (Kapitza and Eppel, 1987). The detailed description of the dynamics and numerics of the model is given by Kapitza, (1987). The turbulent diffusion is parameterized according to the mixing length approach. A sophisticated surface layer module is used for computing the heat and moisture balance at the ground level, taking into account the shortwave and longwave radiation, heat and moisture fluxes in soil etc. The model includes also a cloud module computing mixing ratios of cloud water, rain and cloud ice/snow (combined in one variable) using the 'bulk microphysics' approach.

The original GESIMA does not yet have any 'nesting' subroutines providing time dependent boundary conditions derived from an outer model, so all the initialization and boundary condition procedures involving data from the CMC model had to be written specially for this study.

2.3 The 1989 Project

The adaptation of GESIMA aimed at its coupling with ADOM began in 1989. In the previous project (Niewiadomski, 1989, 1990) the GESIMA simulations were performed in the Toronto area, with the horizontal resolution of 5 km. The domain covered one cell of the CMC grid, with Toronto in its SW quarter. A test run of GESIMA covering the first day of the OSCAR IV period has been completed.

Since this project concerns much larger domain (9 CMC cells, approximately 345km x 345km, with horizontal resolution of 20 km as compared to one cell with 5 km resolution), the results of the last year run cannot be used to drive ADOM, so the GESIMA run must be repeated.

Although most of the modifications of GESIMA introduced during the 1989 project could be transferred to the new, improved version of the model received from Germany for this study, some initialization and boundary condition schemes had to be completely rewritten for this project, due to the much larger domain.

3. MODIFICATION OF GESIMA

The comprehensive description of the GESIMA modifications is provided in the report of the last year project (Niewiadomski 1990). Only the vertical structure of the model and the changes specific to this study are briefly discussed below.

3.1 Initialization

The original model is initialized with horizontally uniform profiles of all parameters. A similar procedure was adopted last year, when GESIMA ran in one cell of CMC grid and could be initialized with uniform profiles derived from the CMC model output. In this study, profiles from 9 CMC cells are available, so different parts of the domain will be initialized with different profiles. To avoid potential numerical instability resulting from horizontal discontinuities of meteorological parameters, and allow their smoother adjustment, the initial period of simulations may require a reduced time step. A similar initialization procedure is planned (but has not been tested yet) for the mesoscale run of ADOM.

3.2 Time Dependent Boundary Conditions

The output of the CMC NWP model is available for each cell of CMC grid with time resolution of 1 hr. These profiles are used to determine the inflow boundary condition for each of four lateral boundaries of the GESIMA domain. First the hourly CMC profiles are interpolated in space, using values from 8 neighbouring CMC cells for each lateral boundary. At each time step of simulation, the inflow boundary values are then interpolated in time for each GESIMA using boundary parameters from the previous full hour and the following one.

A similar procedure is planned for the mesoscale ADOM simulation, with the pollutant fields generated in the large scale ADOM run replacing the meteorological fields from the CMC NWP model.

4. DATA ASSEMBLING AND PROCESSING

In preparation for the GESIMA run, several databases had to be obtained. The data for the particular domain and time period must be extracted from those databases and rewritten in a format acceptable by GESIMA. Most of the data obtained this way will also be used for the mesoscale ADOM run. The software developed for this purpose does not depend on the choice of particular domain, simulation period or horizontal resolution of mesoscale models and will be used in future runs of the nested modelling system. The data bases obtained and the preprocessing software are briefly described below. At the time of writing, the processing of air quality and emissions data necessary for the runs and evaluation of ADOM have not yet begun.

4.1 Meteorological Data

The meteorological fields generated by the CMC NWP model were obtained from the O.M.E. in the form of the input datasets for the 'regular' run of ADOM. Each dataset contains data for the whole ADOM domain, but only one level, so the preprocessing involves mostly the extracting data for the specified mesoscale domain and combining different levels in one profile for each cell. For each mesoscale domain of 3 x 3 CMC grid cells total of 25 hourly profiles of each parameter are needed, since data from the CMC cells adjacent to the mesoscale domain are used to determine boundary conditions.

4.2 Land Use

Land use information is needed in the surface layer submodels of both GESIMA and ADOM to determine surface parameters like albedo, heat capacity, roughness length etc. The data come form an E.P.A. database containing percentages of coverage of a given grid cell by 11 land use categories. The resolution of the EPA grid is similar to that of the mesoscale model but, since the both grids are not identical, the land use data for each mesoscale grid cell have to be interpolated from several (from 1 to 4) cells of the E.P.A. grid.

4.3 Topography

Both GESIMA and ADOM use terrain following vertical coordinates. The topographical data in form of contours in UTM coordinates come from digitized 1:250000 map tapes obtained from the Canada Centre of Mapping of the Energy Mines and Resources Canada. The processing of those data involves extracting the contours from other information, significant reduction of data (since the resolution of 1:250000 maps is much higher than that of the mesoscale model) and converting the contours to average elevations of each mesoscale grid cell. At the time of writing these tasks were well advanced but not yet completed.

5. CONCLUSION

Coupled GESIMA and ADOM models will form a nested mesoscale model capable of simulation of transport, chemical transformations and deposition of atmospheric pollutants with resolution of 20 km or less. The meteorological model GESIMA has been modified to allow its interfacing with ADOM. The necessary data have been assembled and are being preprocessed. The Toronto area run of GESIMA is expected to be completed in the fall 1990. The Toronto runs of ADOM and the runs of both models for the Windsor area will follow. In the future, the area of simulation could cover the entire Windsor- Quebec City corridor.

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AP9

RELATIONSHIP OF SUGAR MAPLE DECLINE AND CORRESPONDING CHEMICAL CHANGES IN SAP CARBOHYDRATES AND TRACE ELEMENTS

D.N. Roy, Saroj Pathak, *Hussain K. Mohamed and T.C. Hutchinson

Faculty of Forestry and Department of Botany
University of Toronto, Toronto, Ontario, M5S 3B3

INTRODUCTION

A systematic chemical information about the sap composition of sugar maple trees, both healthy and declining, is not available in the literature and is not covered by other studies in this field of sugar maple decline research. It is expected that if environmental factors have interfered with the biological processes of a normal maple tree, they would react with the biological and physiological composition of xylem sap carbohydrates, micronutrients and trace elements. The latter would perhaps be reflected in the major chemical components of the xylem sap and stem tissue. Five sample plots, previously established by OMOE as part of its Hardwood Decline Survey Project in 1986, were chosen for site studies. Early (March) and late (April) season sap were collected aseptically from these sites in 1988 and from two of these sites in 1989, and three other sites in 1990. Micro-, macro-elements and trace metals are analysed by AA and ICAP Spectroscopic methods. Mono-, di-, and oligo-saccharides in the sap were investigated by High Pressure Ion Exchange Chromatography (Dionex Corp., Sunnyvale, California). This method of sugar analyses offered a very high resolution (30-100 ppb) for quantitative chemical determination. The method was standardized in our laboratory and provides highly reproducible results. This method has eliminated the uncertainties associated with other existing methods of carbohydrate determination. To provide secondary support for the carbohydrate determination, various other biochemical parameters such as pH, dry weight, and refractive indices of the samples have been recorded for gross estimation. Compilation of data of all these response variables might provide an indication of biological disturbances and corresponding chemical changes taking place in declining maple trees when compared with healthy trees. Work on stem and soil matrices of these trees is also underway as part of a separate study.

We had earlier proposed that at the present stage of our scant knowledge of sugar maple decline, a useful approach might be to study the chemical changes occurring in sap in trees ranging from healthy to declined. The long-term objective being that if we could index the chemical change in xylem sap of declining maple trees, relationships could then be correlated with a physical assessment criterion, Decline Index (DI), recently formulated by OMOE and is currently being used in many related studies. It might further be possible to index these trees chemically much earlier than the onset of the physical decline, thereby facilitating the "early warning" syndrome of maple decline. The focus of this research, therefore, lies in chemical analysis of xylem sap. To the best of our knowledge, this scientific study has not yet been pursued by any other research group involved in sugar maple decline research.

EXPERIMENTAL DESIGN

The sampling unit of this study is an individual (healthy/declining) tree of any of the five sites selected in a NE to SW directional gradient of southern Ontario. Ten sugar maple trees, differing in physical health (as determined by OMOE's DI) and site characteristics (mainly pedological and stand) are selected each from five sites varying in their overall decline status. These sites were mapped out in 1986 as part of the Hardwood Decline Survey, conducted by MOE.

One of these sites has been demarcated as a "base-line site", which will provide a statistically acceptable pattern of variability in levels of sap chemicals. Fifty trees at various stages of decline have been marked for study at this site. This site will further provide data to study the extent of intra-site variability in these trees. All sites selected have been unmanaged for at least the past 17 years, contain at least 50% sugar maple trees, and are situated on the Crown Land, undisturbed by any man-made disturbances. The crossed factorial design of this study includes five sites. Some of the characteristic features and the site DI of these sites are shown in Table 1. Trees were selected so that the healthy trees have DI of <10.00 and declining trees are branded DI of >10 and <90.

TABLE 1

Site Number	Location	Decline Status	DI	Soil Type
AO62	Bancroft 45°20'/78°5'	Healthy	<12.5	Podzolic
AO61	Bancroft 44°50'/78°10'	Severely Declining	>17.5	Podzolic
AO73	Peterborough 44°20'/77°56'	Healthy	<12.5	Calcareous
AO45	Milton 43°32'/80°5'	Severely Declining	>17.5	Calcareous
AO20	Shelbourne 44°5'/80°28'	Moderately Declining	12.6-17.5	Calcareous

Within each category, an attempt was made to include some dominant and some suppressed trees to study the nature and effect of the stand competition on decline.

The present general trend analyses were performed on the basis of these decline categories rather than on the individual numerical values of the physical decline.

Xylem sap at breast heights (1.3 meters) of selected trees have been collected at both early and late sap flow seasons in March and April months of 1988, 1989 and 1990, respectively.

SAP COLLECTION

For sap collection, aseptic conditions were used to avoid metal contamination which might interfere with the trace elemental analyses. A custom designed polyethylene plastic suction apparatus was designed for the extraction of xylem sap in maple trees in the field by MOE. This apparatus was used for the extraction of sap samples in these sites. A two inch hole was drilled by an automatic drill attached onto a chain saw at the south side of the breast height of the trees. A maximum pressure of 120 psi, applied by hand-held lysimeter pump, was enough to yield sufficient sap (30-100) from each tree in 5-20 minutes. As mentioned in the abstract all 90 trees were tapped for sap samples twice during the sap season of 1988 and during 1989, four sap samples were taken from the ten trees of site 45 at weekly intervals and two samples each from ten trees of site 73 were taken at early and late season.

In 1988, a total of 180 sap samples were collected (90 early sap season samples and 90 late season samples from 90 trees). In 1989, 60 more samples were collected (10 each week from site 45 trees for four weeks and 10 early and late samples from site 73 trees). Forty sap samples were collected in 1990. The total volume of collected samples varied between 25-100 mL. Each extracted sap sample was aliquoted and distributed equally in 4 sterile plastic vials (30 mL capacity). The samples were kept cold in the field and frozen at -15°C as soon as possible. The frozen samples were thawed and diluted with deionized water prior to analyses.

ANALYTICAL PROCEDURES

Analyses of Carbohydrates and their derivatives.

Simple sugars and di- and oligo-saccarides were analysed by High Pressure Liquid Ion Exchange Chromatography (HPLIC), a new technique marketed recently by Dionex Corporation (Sunnyvale, California), as BioLC Series 4000i. This is a new chromatographic analysis method utilizing anion exchange separation of carbohydrates with pulsed amperometric detection. Compared to older chromatographic methods with refractive index and ultraviolet detection, anion exchange with pulsed amperometric detection provides specificity, selectivity, sensitivity and reliability. In our laboratory, the chromatograph has been interfaced with a Shimadzu CR5A integrator (Shimadzu Corp., Japan). Sugars in sap were identified and quantified against known standards.

RESULTS

Carbohydrates

Comparison of major pentosans, hexosans and sucrose were undertaken to estimate the relationship of sugar content in sap and degree of decline in maple trees. The experiments were done for both early and late sap samples.

Total Solid Content

Total solids in early and late sap were measured and refractive indices determined by RI measurements to establish the loss of mass.

pH of the Sap

pH of the early and late sap was measured to establish the chemical changes in the sap due to decline and time.

Micro and Macro Nutrients of the Sap

Most of the elements have been analysed by the ICP method. Sodium and Potassium have been analysed by the AA method.

Work in Progress

Analysis of sugars in early and late sap samples collected in the spring of 1989 and 1990 in Milton (Site #45, multiple collection) and Peterborough (Site #73); pH of sap; and micro and macro nutrients are in progress. Statistical analysis will be undertaken after all the experimental data has been collected.

PRELIMINARY CONCLUSIONS

1. Total sugar content and pH decrease as season progresses.
2. Total sugar content and pH are lower in declined trees.
3. As sucrose decreased with decline, proportion of minor sugars increases.
4. Sugar content in the early sap of declined trees is similar to the late sap of healthy trees.
5. *Al, Mn, Fe, Na,* and *Ba* levels are higher in declined trees while levels of *Ca, K,* and *B* are lower.

AP10 Modelling Concentration Fluctuations; E. Alp and A. Ciccone, Concord Scientific Corporation, Downsview, Ontario and C.S. Fung, Environment Ontario, Toronto, Ontario

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VOLUME I

SESSION B

WATER QUALITY RESEARCH

VERBAL PRESENTATIONS

EARLY BIOLOGICAL AND LIFE HISTORY ATTRIBUTES OF THE ZEBRA MUSSEL, Dreissena polymorpha (BIVALVIA: DREISSENIDAE), AND IMPACTS ON NATIVE BIVALVES IN LAKE ST. CLAIR.

G. L. MACKIE

DEPARTMENT OF ZOOLOGY
UNIVERSITY OF GUELPH
GUELPH, ONTARIO N1G 2W1

ABSTRACT

Standing crops of zebra mussels in the Great Lakes are currently increasing by an order of magnitude annually. Zebra mussels already outnumber native species of unionid bivalves by three to four orders of magnitude. They are strongly byssate and with their epifaunal mode of life are colonizing all hard substrates, a habitat that has not been previously exploited by any benthic organism. The species is exhibiting life history features which not only explain why zebra mussels are already the dominant mollusc but indicate that some native species of bivalves may even be eliminated from the Great Lakes. Compared to native species of bivalves, these features include: external fertilization which allows for greater reproduction than internal fertilization; a free-swimming larval stage for more effective and faster dispersal rates (> 250 km yr^{-1} in Lake Erie); a longer (June to October) birth period; up to four orders of magnitude greater recruitment and standing crops; and a faster growth rate. The population of *D. polymorpha* in Lake St. Clair has a different growth rate and life span than do European populations. The Lake St. Clair population is short-lived (2 years), fast-growing (about 2 cm yr^{-1}) and small in adult shell length (less than 3 cm maximum size). Massive encrustations of zebra mussels are hypothesized to have one or more of the following effects on native unionid clams: (i) impairment of normal locomotion and burrowing activities; (ii) prevention of valve closure by invasive growth of zebra mussels thus exposing the unionid to predation, parasitism and environmental extremes; (iii) prevention or limitation of valve gaping to affect normal metabolic functions for feeding, growth, respiration, excretion and/or reproduction; (iv) interference of normal functioning of the siphons and processes associated with them (e.g. respiration and feeding); (v) stripping the water of food and nutrients making little or none available to the unionid host which may ultimately starve to death; (vi) cause shell deformities that may ultimately result in premature death of the unionid; (vii) smothering by complete occlusion of the siphon region.

INTRODUCTION

The zebra mussel is a new bivalve that was introduced into the Great Lakes three years ago in the freshwater ballast of ocean-going ships from Europe (Hebert et al 1989). In the worst-case scenario, it has the potential to not only become the most serious and devastating pest of any exotic species ever introduced to North American surface waters, but also to completely alter the ecology of the Great Lakes. For more than 100 years the Europeans have witnessed its ability to (i) clog intakes and distribution pipelines in industrial and domestic facilities; (ii) corrode steel and iron pipes; (iii) taint and contaminate potable water supplies; and (iv) encrust hulls of boats and ships (Morton 1969a; Mackie et al 1989). In only three years, utilities, industries, water treatment plants and boaters on Lake Erie and Lake St. Clair have already seen these effects and, in addition, have documented: (v) fouling and rendering useless fishing gear and navigational aids (e.g. buoys); (vi) reduction, or possibly elimination, of the recreational and aesthetic value of beaches and shorelines; (vii) potential displacement of native species of bivalves; (viii) alteration or even destruction of fish habitats; and (ix) changes in the physical limnology (e.g. Secchi depth) of infested lakes (Lakes Erie and St. Clair).

The epicentre of zebra mussel invasion for the Great Lakes, and ultimately for all North American surface waters, is Lake St. Clair (Hebert et al 1989) where three generations now flourish. We anticipate that the standing crop of this newly introduced species will continue to increase during its early colonization phase, and then crash to a base level. This paper reports the current standing crop of zebra mussels in Lake St. clair and the apparent increase in their numbers since 1988 when Hebert et al (1989) described the first record. Since Lake St. Clair is the epicentre of dispersal for the zebra mussel, the lake will form an excellent model for predicting the biology, ecology and impact of the zebra mussel in other lakes. The objective of this study is to collect baseline data to determine annual changes in size, age and growth rate of the population, size, age and growth rate of individuls, sex ratio, fecundity, birth period(s), larval development and growth rate, dispersal rate and the impact on native species of Unionidae bivalves. These data will be used in models to determine the time required to attain peak population standing crop (i.e. the population "explosion" period), the maximum standing crop attained, the time to attain the minimum population standing crop (i.e. population "crash" period), the minmimum standing crop attained, the mean population standing crop attained, and the short term (1 to 3 years) and the long term impact of zebra mussels on the native unionid bivalves of the Great Lakes.

METHODS

At two week intervals from May 2, 1989 to September 15, 1989, then monthly in October, November and December, 1989, 3 to 5 rocks were collected from Lake St. Clair at Puce, Ontario. The rocks varied in size from approximately 5 cm diam to 30 cm diam. Each rock was considered a sampling unit (replicate). All mussels were scraped off the rocks. At each sampling event, 10 to 20 individuals representing all length classes were randomly selected from one or all of the rocks and fixed immediately in Bouin's fluid for histological examination of gametogenesis and sex ratio; 75 to 100 individuals representing all size classes were randomly selected from one or all of the rocks for determining length-dry weight (on fresh specimens) relationships; and the remainder were preserved in 70% ethanol for deriving length-frequency histograms. The histograms were used to determine: (i) population age and size class structure; (ii) mean growth rate of each age class (cohort); (iii) life span; and (iv) birth period. The growth rate of the 1989 cohort was determined by placing a cement block in 0.6 m of water and measuring at two week intervals the increase in growth in shell length of newly settled mussels.

The mean population size at each time interval was determined by enumerating the mussels on each rock surface. The surface area of the rock was determined by placing aluminum foil around the part of the rock surface that was infested with mussels. The foil was pressed into crevices and around protuberances and any excess foil in folds resulting from this procedure was cut off. The foil was removed from the rock and the area of the foil was determined with a planimeter. The standing crop on each rock (sampling unit) was expressed as number per square metre.

The birth period was also determined by the appearance of larvae collected in student plankton samplers (mouth 20 cm diam, mesh 70 u) taken at the same sampling intervals as for adult mussels. The plankton sampler was simply swept back and forth several times in the top 0.3 m of water and the plankton collected was preserved in 5% formalin. Two of these samples were collected, followed by three, 15-L Schindler-Patalas trap samples for determining the mean abundance of veliger larvae in the water.

The sex ratio was determined from histological examination of 40 specimens fixed in Bouin's fluid. Soft tissues were removed from the shell, embedded in wax, sectioned at 6 um using a Spencer model 820 microtome and stained with Harris' modified hematoxylin and counter stained with eosin, following methods in Humason (1982). Only the posterior part of the visceral mass containing the gonad was sectioned. The period of gametogenesis and length class at which gametogenesis begins were determined from histological examination of three specimens in each of four length classes (0 to 5 mm; 5 to 10 mm; 10 to 15 mm; and greater than 15 mm) in biweekly collections of mussels beginning May 2, 1989 and ending September 22, 1989.

Only superficial effects of zebra mussels on unionid clams were examined in 1989. The relationships between unionid size and zebra mussel abundance and size was determined by removing and counting all the mussels, measuring the shell length of at least 50 mussels selected at random from each unionid shell, and then plotting the number and mean length of the zebra mussels against the shell length of the unionid. Curvilinear regressions were calculated for each plot using SAS software.

The dispersal rate of zebra mussels upstream and downstream of Lake St. Clair was determined from the appearance of larvae in zooplankton samples and newly settled adults on concrete blocks at each of twelve stations: Bright's Grove on Lake Huron; Corruna and Port Lampton on the St. Clair River; Stoney Point, Belle River and Puce in Lake St. Clair; Amherstburg in the Detroit River; Wheatley, Port Stanley, Port Dover, Long Beach in Lake Erie; and Niagara-on-the-lake in lake Ontario. Zooplankton samples were taken with a student plankton sampler with 20 cm diam mouth and a nylon mesh with 70 u mesh openings. The concrete blocks measured 10.16 cm high, 20.32 cm wide and 40.64 cm long (4 in X 8 in X 16 in) and were placed in 0.6 m of water at each each station. Zooplankton samples were taken and concrete blocks were examined at two week intervals beginning May 15 and ending November 15, 1989.

RESULTS AND DISCUSSION

The population size class structure of *Dreissena polymorpha* in the summer and fall of 1989 in Lake St. Clair is shown in Figs. 1a to 1g. Three distinct cohorts are present through most of the year, the dominant age class being one-year olds. The smallest individuals appear on two occasions, once in the late spring to early summer (late June to early July) and again in late October to early November, suggesting two annual recruitment events (birth periods), although recruitment is continuous throughout the summer. The disappearance of the oldest (largest) age class by mid summer suggests that most individuals live only three years in Lake St. Clair. This is intermediate between native sphaeriid bivalves (a few months to two years (Mackie 1989)) and unionid clams (up to twenty years Clarke 1973)). Moreover, the birth period of sphaeriid bivalves is usually confined to a few weeks in the summer (Mackie 1989) and of unionid clams to either the spring or summer (Clarke 1973).

The growth rate curves of each age class (cohort) are shown in Fig. 2, with the dates representing the time of birth. The spring 1989 cohort was born on June 27, 1989 (57 days) and grew almost 2 cm by November 15, 1989 (194 days), with a mean growth rate of 0.126 mm day^{-1}. The fall 1988 cohort also added nearly 2 cm in shell length within 194 days, but averaged only 0.100 mm day^{-1}. However, during the log phase of growth, the maximum growth rates of both the fall 1988 and the spring 1989 cohorts were similar, averaging nearly 0.5 mm day^{-1}. The cohort born in the spring of 1988 (apparently) also had similar rapid rates of growth and peaked, but the cohort died at the end of July, indicating that the cohort lived for only a year and a half. The 1987 cohort (apparently) was probably born in the summer or fall of 1987, giving that cohort a life span of only two years. Hence, the data suggest that the life span of *D. polymorpha* in Lake St. Clair is only two years maximum.

The data from this length-frequency analyses are supported by data obtained from the growth of mussels settling on concrete blocks placed in the water during the first week of June (Fig.2). Growth is most rapid in newly settled and first-year individuals and decreases with increasing age, which is typical for the species (Morton 1969b; Stanczykowska 1977).

The age and growth rate of *D. polymorpha* in Lake St. Clair are different than reported for European populations. The life span of zebra mussels in Europe varies between 3 (e.g. Stanczykowska 1977) and 5 years (e.g. Wiktor 1963; Stanczykowska 1964) in Polish lakes; 5 years in British reservoirs (Morton 1969b); 6 and 7 years in Swiss lakes (Stanczykowska 1977) and 6 and 9 years in some Russian reservoirs (Mikheev 1964; Lyakhov and Mikheev 1964). These variable life spans can be categorized into two groups. The first group is slow-growing, has a maximum shell length of 3.5 cm or less and is characterized by populations that live for 3 to 5 years. The group is typical of populations in Poland, Austria, Hungary, Switzerland and Russia (Mackie et al 1989). The second group is fast-growing, has a maximum shell length greater than 4 cm and is characterized by populations that live for more than 5 years. This group is typical of populations in Britain (Mackie et al 1989). The population of *D. polymorpha* in Lake St. Clair seems to be most similar to the first group of short-lived (2 years), fast-growing (about 2 cm yr^{-1}), small adults (less than 3 cm maximum size).

The allometry of shell growth is shown in Fig. 3. Shell width is described by the relationship, width = 0.048 + 0.488 length ($r^2 = 0.99$). Shell height is described by the relationship, height = 0.161 + 0.208 length + 0.072 $length^2$. The length-weight relationship is typical of most animals with a cubic relationship: total weight (mg) = 0.051 $length^{2.996}$; tissue weight = 0.007 $length^{2.982}$ (Fig. 4). The allometry of shell growth is within the variations reported for British (Morton 1969b) and Polish (Stanczykowska 1977) populations of *D. polymorpha*. In Europe the length-weight relationship varies considerably among lakes (Lyakhov and Mikheev 1964; Walz 1978 a, b; Stanczykowska 1979) and over time (Stanczykowska et al 1975) and may be an indicator of environmental conditions (Stanczykowska 1979).

The mean standing crop of zebra mussels on rocks before the 1989 recruitment event (i.e. before settlement of youngest age class) was 10,045 m^{-2} (std. dev. = +/-5450 m^{-2}, range = 2,835 to 209,360 m^{-2}). The mean standing crop of mussels on unionid clams before the 1989 recruitment event was 7.86 cm^{-2}, or 78,600 m^{-2} (std. dev. = +/-10,575 m^{-2}, range = 400 to 450,500 m^{-2}) of posteriorly-exposed shell per unionid. There are significantly ($P < 0.05$) more zebra mussels on unionid clams than on rocks on a unit area basis. Regardless of which estimate is used, the mean standing crop of zebra mussels is two to three orders of magnitude greater than that of sphaeriid clams (range 20 to 125 m^{-2}, Griffiths (1987)) and three to four orders of magnitude greater than that of unionids (range 1 to 10 m^{-2}, this study and Griffiths 1987)).

Hebert et al (1989) reported a mean abundance of about 20 mussels on 10-cm long unionid shells in Lake St. Clair in 1988. In 1989, the mean abundance of zebra mussels on 10-cm long unionid clams was about 250, a 12.5 fold increase since 1988. Based on these data, the population of zebra mussels in lake St. Clair increased by at least by an order of magnitude (i.e. 10X) in one year. The mean length of unionids in Lake St. Clair in 1989 was about 8.5 cm and they supported an average of nearly 210 zebra mussels per shell (Fig. 13). The mean standing crop of unionid clams in Lake St. Clair is about 6.7 m^{-2}, yielding an average standing crop of "unionid supported" zebra mussels of 1,407 m^{-2}.

Based on histological examination of 40 specimens, the sex ratio of *D. polymorpha* in Lake St. Clair in 1989 was 3:2. Gametogenesis had already begun and gonads were ripe with both eggs and sperm in the first (May 2) collection of the year (Figs. 5, 9), suggesting that gametogenesis began in the winter or early spring. In European populations, oogenesis begins in the fall, followed by intensive growth of the oocytes in early spring (Antheunisse 1963). The sex ratio of most Polish populations of *D. polymorpha* is 1:1 (Stanczykowska 1977). Compared to native bivalves, most unionid species also have sex ratios of 1:1 (Clarke 1973); sphaeriids are hermaphroditic (Mackie 1989).

In the ovary the average size of a ripe egg is 50 um diam. The eggs possess a clear nucleus of 30 um diam and a nucleolus of 10 um diam. The immature eggs are attched to the epithelial wall of the follicle by a stalk. The diameter of the stalk decreases as the eggs ripen. When the egg is ripe it detaches from the wall of the follicle and lies free in the lumen of the ovarian follicle (Fig. 5). The micropyle denotes the point of attachment of the stalk to the wall of the follicle. Some eggs are released from the ovaries in late May (Fig. 6) but the peak period of reproduction is in July and August when most ovaries appear partially spent (Fig. 7). The ovaries are completely spent by the end of September (Fig. 8).

All stages of spermiogenesis are present by early May (Fig. 9). The enlarged semeniferous tubules contain primary and secondary spermatocytes, spermatids and mature spermatozoa. Ripe semeniferous tubules have an average diameter of 150 - 200 um. The sperm have elongated heads, averaging about 3 um in length. Ripe spermatozoa are located near the lumen of the seminiferous tubule with the tails directed toward the lumen (Fig. 9). Release of sperm appears to begin in late May (Fig. 10) but most are released by July and August (Fig. 11). The semeniferous tubules are completely spent by late September (Fig. 12).

Reproduction begins when specimens are about 5 mm in length and is complete before they reach 10 mm shell length. Nine of 12 specimens examined in the 5 to 10 mm length class were sexually mature. A greater proportion (12 of 13) of individuals in the 10 to 15 mm length class were ripe than in the 5 to 10 mm length class. In European populations, gametogenesis begins in adults of slightly larger sizes of 8 - 9 mm in shell length (Morton 1969b; Stanczykowska 1977).

Veliger larvae first appeared in Lake St. Clair (at Puce, Belle River and Stoney Point) and Lake Erie (at Wheatley) in June 14 samples. None were found in the May 28 samples, indicating that the veliger larvae appeared in both lakes sometime between May 28 and June 14, 1989. This birth period is similar to most populations in Europe (Stanzcykowska 1977). The abundance of veliger larvae was not determined in 1989, but the absence or low numbers of < 1 mm length adults in late July to mid August of the length frequency plots (Fig. 1) suggest that there were two recruitment events, one in the spring and another in the late summer. If veliger larvae require one month to develop and settle, the larger numbers of small mussels in early July settled from the reproductive event in June and the large number of small mussels in September to November settled from the reproductive event in late July to mid August.

Dreissena polymorpha is the only freshwater bivalve in the Great Lakes that produces free-swimming veliger larvae. Sphaeriid clams are ovoviviparous, brooding their young in brood sacs on the inner gill of the parent, and producing 1 to 5 newborn (usually) (Mackie et al 1978). Unionids brood glochidia in marsupia on the inner or outer gill, or both. Most species of unionid clams require a fish host for the parasitic glochidia to develop into the juvenile stage (Clarke 1973).

The infestation intensity increases with length (Fig. 13) and posteriorly exposed surface area (Fig. 14) of the unionid in a logarithmic relationship. Living unionid clams have an average infestation of about 210 (+/- std. dev. 56) zebra mussels per unionid (estimate based on counts made before the 1989 recruitment event) (Fig. 13). All eight species of unionids (living shells) found had zebra mussel infestations (Fig. 15). When the exposed surface of the unionid is covered, new recruits settle on top of older recruits so that the infestation intensity increases on larger unionids. Some infestations are invasive and prevent the unionid from closing its valves (Fig. 16a). Other infestations are so great that it was difficult to completely open the valves of empty shells or moribund individuals (Fig. 16b).

Some unionid shells carry more than 2800 zebra mussels with an average length of 4.5 mm. Using the length-weight regression given earlier, the biomass of zebra mussels supported by these unionid shells is 11.5 g (dry weight). The unionid itself weights 21 g (dry weight, indicating that some unionids are carrying more than half their weight. Indeed, some unionid shells support more than 15,000 zebra mussels (Hebert, pers. comm.) suggesting that, in extreme cases, some unionid shells are supporting up to three times their own weight. This observation, and others made earlier, suggest that the massive encrustations of zebra mussels will: (i) impair normal locomotion and burrowing activities; (ii) prevent valve closure by invasive growth of zebra mussels thus exposing the unionid to predation, parasitism and environmental extremes; (iii) prevent or limit valve gaping which may possibly affect normal metabolic functions for feeding, growth, respiration, excretion and/or reproduction; (iv) interfere with the normal functioning of the siphons and processes associated with them (e.g. respiration and feeding); (v) block the siphonal region and eventually smother the unionid; (vi) strip the water of food and nutrients making little or none available to the unionid host which may ultimately starve to death; and (vii) cause shell deformities that may ultimately result in premature death of the unionid. These negative effects do not support the conclusions of Lewandowski (1976) who found no "unfavourable" effects of zebra mussel infestations on Unionidae in Polish lakes.

When the concrete blocks were placed in the lakes in the spring of 1989, the zebra mussel had already been found as far east as Port Stanley in Lake Erie and as far west as Stoney Point in Lake St. Clair. By November, mussels were found on blocks as far east as Niagara-on-the-lake but had not been found on any blocks further west or north than Stoney Point in Lake St. Clair where they were already established. On this basis, downstream dispersal occurred at a rate of approximately 250 km yr^{-1}. Upstream dispersal was negligible within the area under study.

The zooplankton samples confirmed all the results obtained from the concrete blocks. Veliger larvae were found two weeks earlier than adults at Port Dover (August 8, 1989) and Long Beach (September 22) in Lake Erie and on the same week at Niagara-on-the-lake (November 22, 1989). Since samples were taken at two week intervals in the summer and monthly in the fall the veliger larvae (and adults) may have actually appeared two weeks earlier at Port Dover and Long Beach and one month earlier at Niagara-on-the-lake.

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CAPTIONS TO FIGURES

Fig. 1. Length-frequency distribution of Dreissena polymorpha in Lake St. Clair between May 2 and November 22, 1989.

Fig. 2. Growth rates of cohorts of Dreisseina polymorpha based on data in Fig. 1. Dates represent time of birth for the cohort. See text for details.

Fig. 3. Allometry of shell growth in *Dreissena polymorpha* in Lake St. Clair.

Fig. 4. Length-weight relationships of *Dreissena polymorpha* in Lake St. clair.

Fig. 5. Section through ovary of *Dreissena polymorpha* collected May 2, 1989 from Lake St. Clair.

Fig. 6. Section through ovary of *Dreissena polymorpha* collected June 22, 1989 from Lake St. Clair.

Fig. 7. Section through ovary of *Dreissena polymorpha* collected August 14, 1989 from Lake St. Clair.

Fig. 8. Section through ovary of *Dreissena polymorpha* collected September 22, 1989 from Lake St. Clair.

Fig. 9. Section through testis of *Dreissena polymorpha* collected May 2, 1989 from Lake St. Clair.

Fig. 10. Section through testis of *Dreissena polymorpha* collected June 22, 1989 from Lake St. Clair.

Fig. 11. Section through testis of *Dreissena polymorpha* collected August 14, 1989 from Lake St. Clair.

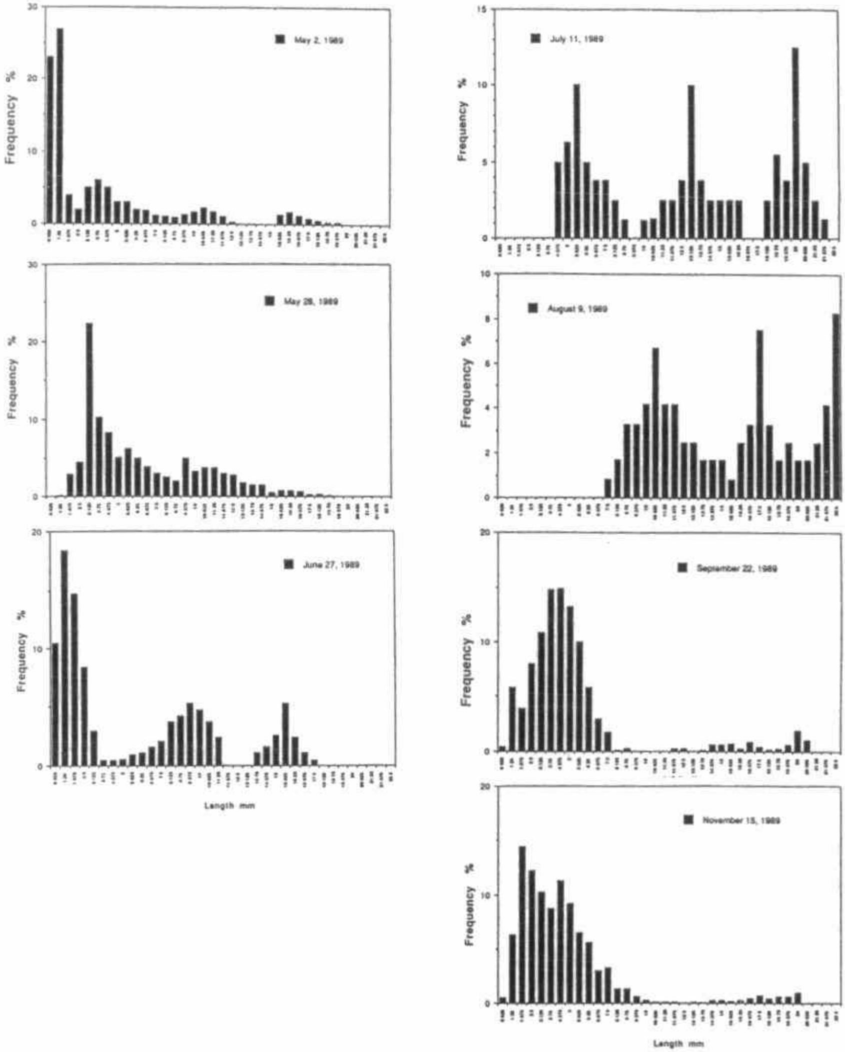
Fig. 12. Section through testis of *Dreissena polymorpha* collected September 22, 1989 from Lake St. Clair.

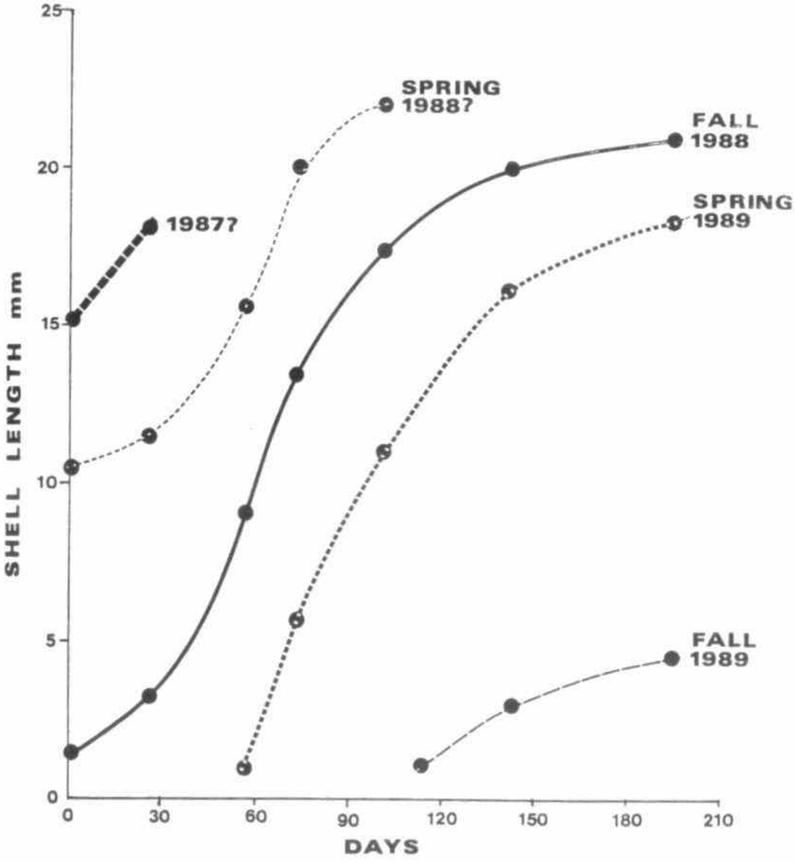
Fig. 13. Relationship between length of unionid and number of zebra mussels attached to its shell.

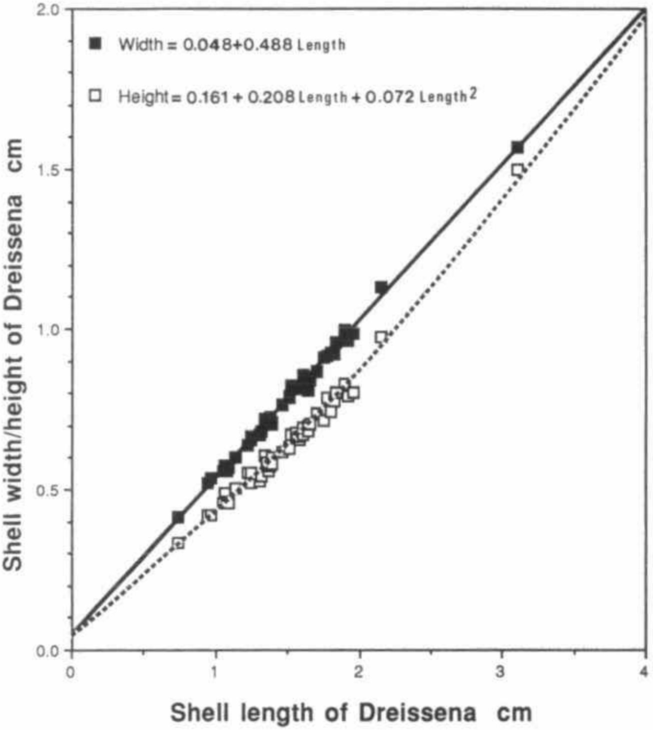
Fig. 14. Relationship between posteriorly exposed surface area of unionid shells and numbers of zebra mussels attached.

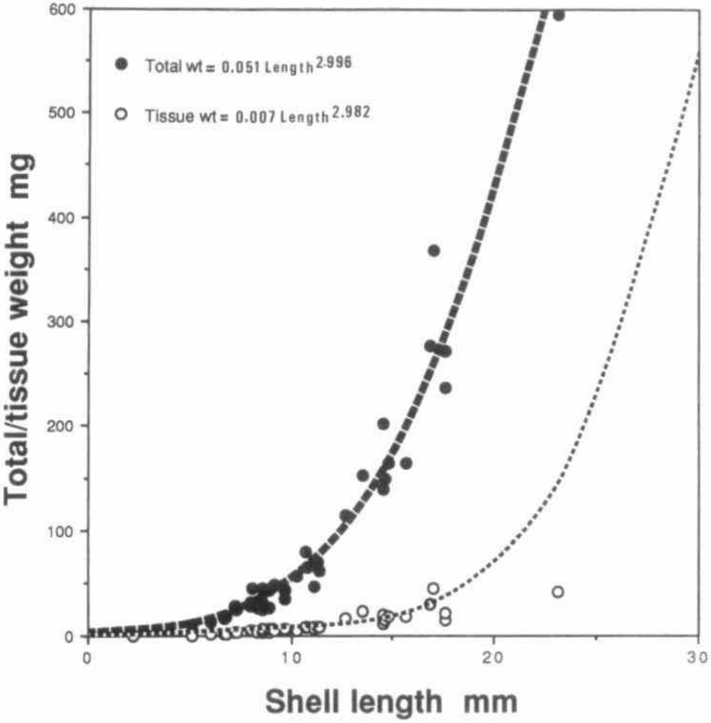
Fig. 15. Eight species of unionids from Lake St. Clair with zebra mussel infestations. (a) *Proptera alata*; (b) *Leptodea fragilis*; (c) *Ligulia recta*; (d) *Lampsilis radiata*; (e) *Elliptio dilatata*; (f) *Lasmigona complanata*; (g) *Pleurobema coccineum*.

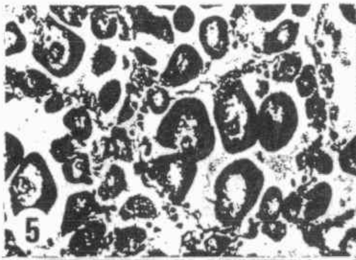
Fig. 16. (a) Infestations by zebra mussels so intense that unioind cannot close its valves. (b) Infestations by zebra mussels so intense that unionid valves cannot be opened.


May 2, 1989
Frequency %
30
20
10
0
May 28, 1989
Frequency %
30
20
10
0
June 27, 1989
Frequency %
20
10
0
Length mm
July 11, 1989
Frequency %
15
10
5
0
August 9, 1989
Frequency %
10
8
6
4
2
0
September 22, 1989
Frequency %
20
10
0
November 15, 1989
Frequency %
20
10
0
Length mm


SHELL LENGTH mm
0
5
10
15
20
25
DAYS
0
30
60
90
120
150
180
210
1987?
SPRING 1988?
FALL 1988
SPRING 1989
FALL 1989


■ Width = 0.048+0.488 Length
□ Height = 0.161 + 0.208 Length + 0.072 Length2
Shell width/height of Dreissena cm
Shell length of Dreissena cm
0.0
0.5
1.0
1.5
2.0
0
1
2
3
4


600
500
400
300
200
100
0
● Total wt = 0.051 Length$^{2.996}$
○ Tissue wt = 0.007 Length$^{2.982}$
Total/tissue weight mg
0
10
20
30
Shell length mm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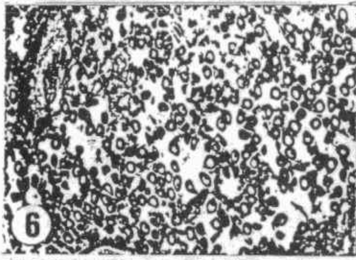
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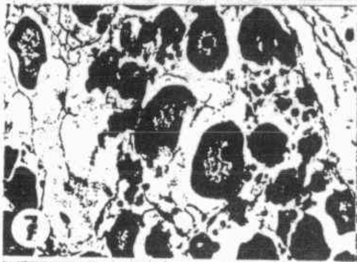
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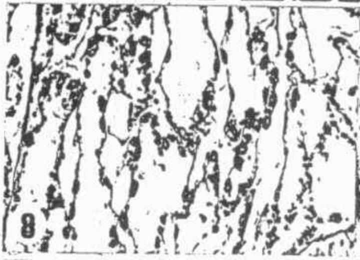
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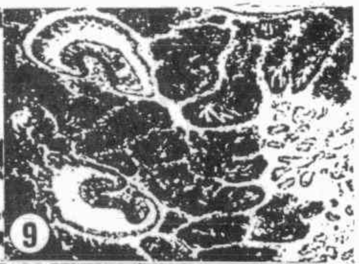
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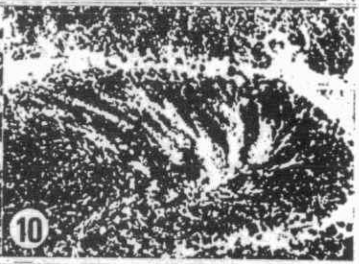
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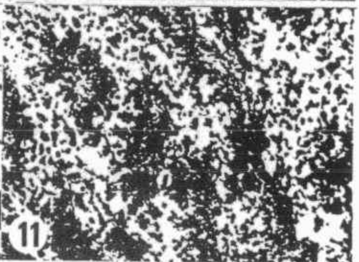
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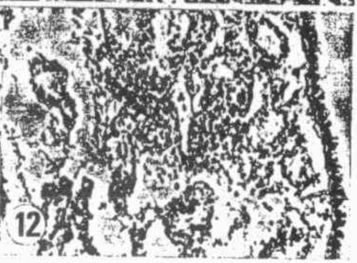
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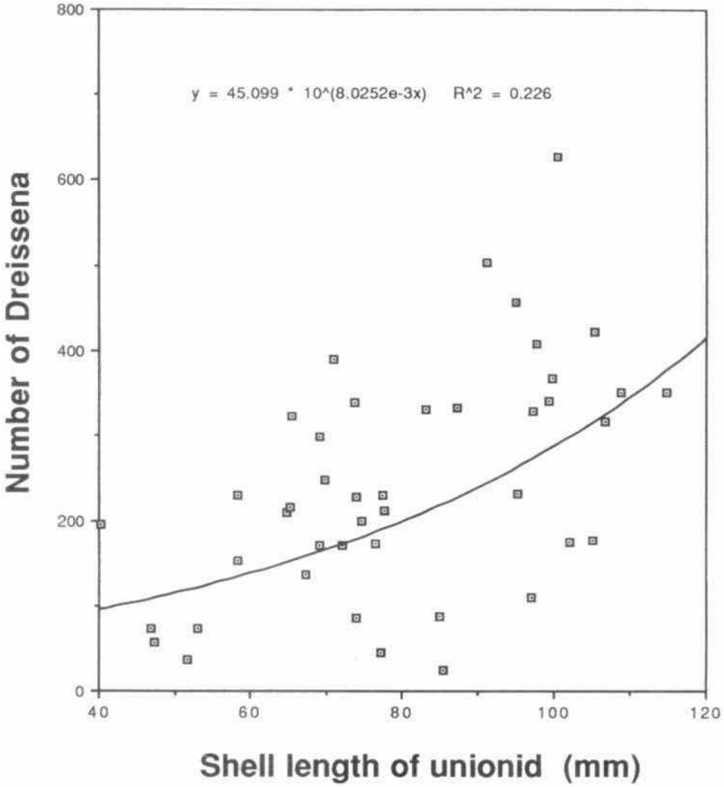
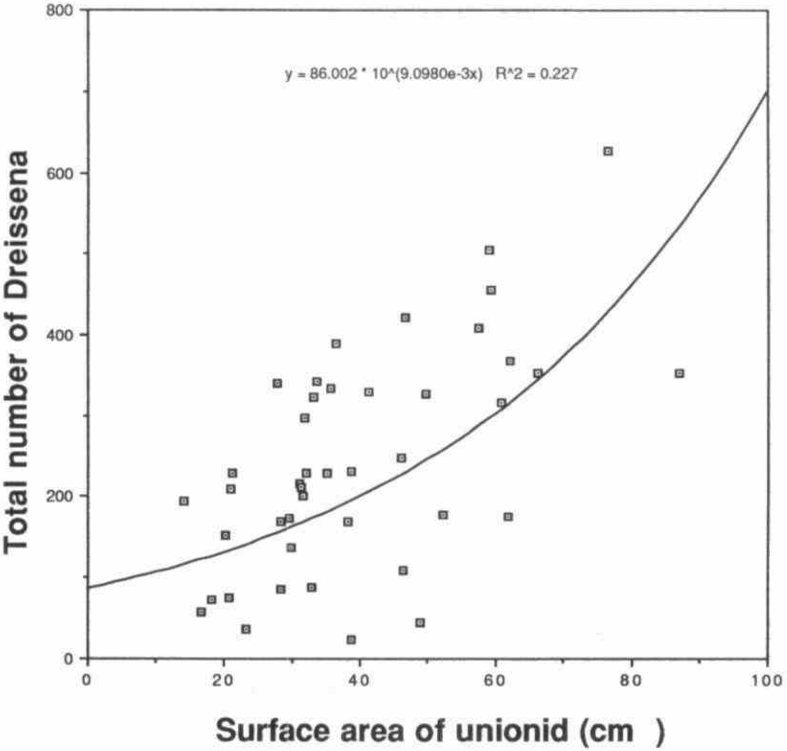
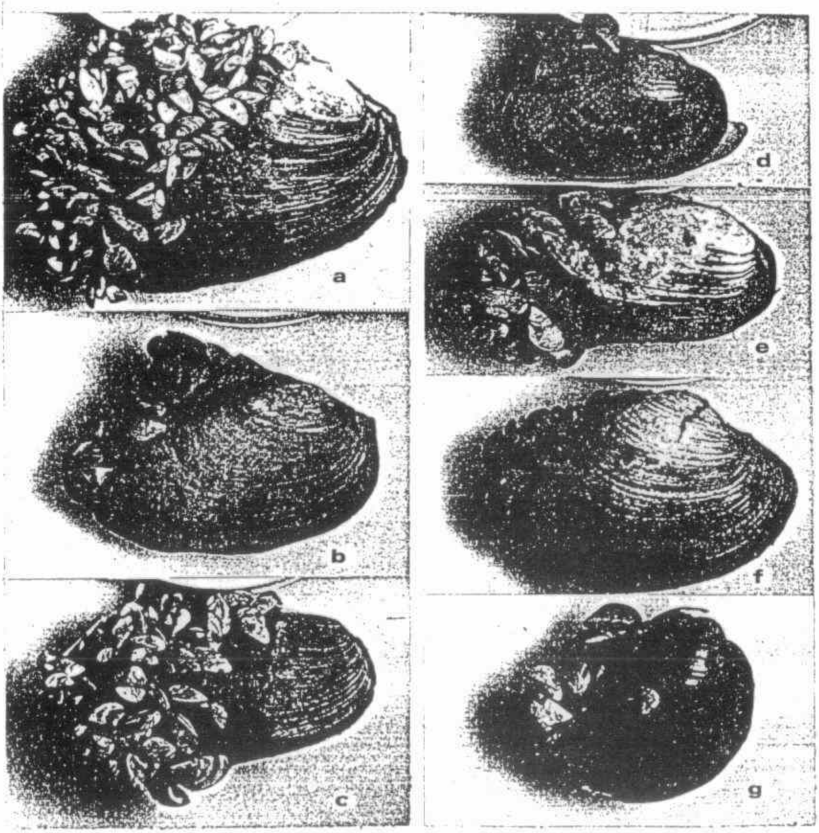
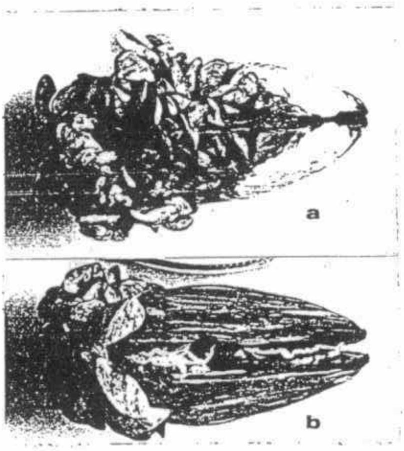

y = 45.099 * 10^(8.0252e-3x) R^2 = 0.226
Number of Dreissena
800
600
400
200
0
40
60
80
100
120
Shell length of unionid (mm)


y = 86.002 * 10^(9.0980e-3x)   R^2 = 0.227
Total number of Dreissena
0
200
400
600
800
0
20
40
60
80
100
Surface area of unionid (cm)


a
b
c
d
e
f
g


a
b

B3

TOXICOKINETIC MODELLING OF MIXTURES OF ORGANIC CHEMICALS

L.S. McCarty*, G.W. Ozburn, A.D. Smith, and D.G. Dixon■

Aquatic Toxicity Research Group, Lakehead University, Thunder Bay, Canada, P7B 5E1

■ Biology Department, University of Waterloo, Waterloo, Canada, N2L 3G1

* CanTox Inc., 627 Lyons Lane, Oakville, Canada, L6J 5Z7

INTRODUCTION

Problems associated with examination of the combined effects of toxicants have been the topic of several recent reviews (U.S. EPA, 1986; de March, 1987 a&b; Hermens, 1989; Christensen and Chen, 1989). Current approaches to dealing with mixture toxicity are based on various methods of examining "indexes" based on results largely from the mixture toxicity methodology discussed by Sprague (1970) as the "toxic unit" model. Ideally, "threshold" toxicity estimates, obtained when time and kinetic factors have been eliminated, are employed in the toxic unit equation. However, much of the aquatic bioassay data used is based on fixed duration exposures where threshold has not been confirmed or where exposures, although chronologically identical, have not been confirmed to be toxicologically similar, contrary to Sprague's advice. This approach is subject to further complications when it is used to study mixtures, **as it is a static approach to what is essentially a dynamic problem.** In other words, the method compares toxicity estimates obtained from bioassay data, obtained at fixed exposure durations, and ignores a very important aspect of the toxicological process, the time course of both accumulation and toxic action (Tichy and Roth, 1988), which may be particularly problematic in mixture toxicity.

As has been noted by Sprague (1970) threshold is relatively simple to determine with single toxicants. In a mixture, the overall time-course of toxic action is affected by the kinetic factors controlling net accumulation of each component. If net uptake proceeds at different rates for each chemical, the contribution of each to the total critical residue will vary with time. Also, each will achieve its respective threshold at a different time. Thus, the toxicological effects of a mixture through time may be complicated and different than that exhibited by any of its individual components. Although time may also influence toxicodynamics as well as toxicokinetics, for the sake of simplicity it has been assumed that the biological response occurs very shortly after a critical residue has been reached in the organism.

Although useful information can be obtained with proper implementation of the basic toxic unit approach or related mixture indexes, a method which incorporates exposure time and kinetics would be even more informative and begin to address the concerns of fate and toxicity modellers who must deal with time as a significant modifying factor. The one-compartment, first-order kinetics (1CFOK) model of bioaccumulation, in conjunction with the critical toxicant body residue relationships discussed elsewhere (McCarty *et al.*, 1989; McCarty 1990) should provide a more useful and informative approach. Although a similar kinetics-based development could be applied to the basic toxic unit concept, it is still "black box" in nature as little of the processes occurring in the organism are examined. The residue-based approach is easier to manipulate and both the exposure water concentrations and the residues modelled can be subjected to quantitative hypothesis testing. In this paper the simplest case, the toxicity of mixtures of chemicals with a similar mode of toxic action - similar joint action - has been considered. There are two main advantages. Firstly, for the same mode of toxic action, and similar organism characteristics, a molar concentration of a mixture should produce a similar biological response to that produced by the same molar concentration of a single chemical. For narcosis with chemicals with a log Kow greater than about 1.5 this appears to be about 2 to 6 mmol toxicant per L of fish, for small fish of about 5% lipid (McCarty, 1986, 1987, 1990; Abernethy *et al.* 1988). Secondly, the contribution of each component of the mixture to the toxic response can be followed with time. Various biological factors (size, lipid content etc.) and chemical-physical factors (hydrophobicity, pKa etc.) which influence kinetics can also be examined and be accounted for, although the latter aspect will not be addressed herein.

The objective of this paper is to model, based on 1CFOK model assumptions, the time-course and ultimate body residue at lethality for several mixtures based on data from toxicity tests with single organic chemicals. The success of the mixture modelling will be determined by comparison to bioassay results independently observed in actual mixture toxicity bioassays. The lack of measured body residues in this data set has made the task somewhat more complicated. Therefore it should be viewed as a feasibility study carried out with data not expressly obtained for this purpose. The variability may be higher than might be normally considered acceptable; on the other hand, if a trend is apparent despite the variability, it suggests that the concept is robust. In addition to data for narcotic organic chemicals, a bioassay of a mixture of 3 "polar narcotics" was available. Although complicated by the problems of ionization, and the fact that the chemicals in the mixture have dissimilar modes of action, an attempt was made to apply a similar, residue-based kinetics analysis to it.

DATA

The results of acutely toxic exposures of American flagfish, *Jordanella floridae*, (≈0.5-4 g, ≈10% lipid, ranging from 7-16%, typically 8-13%) with a variety of single chemicals and their mixtures carried out by the Aquatic Toxicity Research Group of Lakehead University (ATRG, 1987, 1988; Smith *et al.*, 1990, in press). An evaluation of the mixture toxicity of this data, based on a toxic unit analysis of 96-h LC50 data for the components of the four mixtures examined is presented below (ATRG, 1987, 1988). All seem sufficiently close to unity to conclude that these compounds are simply additive.

Triple Chlorobenzene mixture TU = 1.12 (1.01-1.24)
Double Chloroethane mixture TU = 1.11 (1.05-1.18)
Double Chloroethylene mixture TU = 1.09 (0.91-1.32)
Triple Chlorophenol mixture TU = 0.90 (0.81-1.00)

The chlorobenzene mixture experiment was problematic as the ratios between the concentrations in the 9 exposure concentrations were not constant (ATRG, 1987). The TU value for this has been recalculated herein using the three exposure levels where the ratio of the three components averaged 63%, 28%, and 9% of the respective 96-h LC50 for DCB, TCB, and TeCB. The fourth level used to estimate the TU LC50 was the next lowest exposure level with no mortality.

METHODS AND RESULTS

Deriving 1CFOK Modelling Parameters

Table 1 summarizes the parameters which have been derived for 1CFOK modelling; they have been obtained from several sources. Two critical factors, the elimination rate constant k2 and the threshold LC50 water concentration (Cw_{∞} or BCF/Cf_R) have been estimated by non-linear curve fitting to the raw time toxicity data (McCarty *et al.*, 1989). As noted elsewhere (McCarty, 1990), the non-linear curve fitting process is subject to statistical problems (pseudoreplication), yet more statistically valid alternative procedures are also limited by the nature of the data. Nevertheless, it is not possible to completely solve a 1CFOK model equation without at least one additional parameter (Mancini, 1983). This can be either a measured body residue for fish that have died, or a measured k1, the uptake rate constant, or a measured BCF. There are two methods of estimating a solution to this problem. The first is to estimate a BCF from established relationships between log Kow and BCF, taking into consideration the influence of lipid content on BCF. K1 and a critical body residue can then be calculated from the existing information. The second is to use an estimated critical body residue derived from another source and adjust it for lipid content. With this information k1 and BCF can be calculated from existing information.

Aspects of both approaches will be used. The first approach will be used to estimate the necessary kinetics parameters and body residues for the single chemical bioassays. BCF values, calculated from Mackay's (1982) Kow-BCF relationship using log Kow values from the MEDCHEM CLOGP 3.5 database and adjusted to 10% body-lipid content (i.e. BCF=0.10*Kow) to reflect the higher lipid content of these fish, were used to solve the 1CFOK equation. The calculated BCF values were used for consistency of approach across the three narcotic chemical groups examined. In the case of chlorobenzenes, BCFs were also measured independently in bioconcentration tests. These values were in good agreement with ones calculated from log Kow (331, 1050, 6610 versus 295, 2040, 4070, respectively). As noted in Smith *et al.* (1990), the elimination half-life for these chemicals in flagfish is similar, whether estimated from toxicity or bioconcentration bioassay data. K1 was obtained by estimating it from BCF since k1/k2 = BCF. The critical body residues presented in Table 1 were estimated as the product of calculated BCF and LC50.

The critical body residue data (mean and prediction range) obtained earlier with the fathead minnow narcotics data set - approach 2 - will be used as independent verification of the validity of the model for the three mixtures of narcotics. As well, the range of critical residue data will be used to produce model prediction limits which will be compared to the results of independently observed mixture toxicity bioassays. The adjustment for the higher lipid content of flagfish also extended to the critical body residue level. As the American flagfish were about double the lipid content of the fathead minnows, the estimated critical body residues estimated for fathead minnows (McCarty, 1990) were also doubled to 8.6 mmol/L (4.4-16.2) to approximate flagfish critical body residues. This does not indicate that the target concentration or target size has changed, just that the steady-state level fish level will be higher as there is more lipid for toxicant to partition into. As can be seen in Table 1, the estimated critical body residues for single narcotic exposures fall into this range, with the exception of 1,1,2-trichloroethane which is slightly below it.

Table 1: Information Used for Modelling the Exposure of American Flagfish to Some Organic Chemicals

Chemical	Threshold LC50 mmol/L	k2 h-1	BCF*	k1* h-1	Estimated Fish Residue* mmol/L
1,4,-dichlorobenzene	0.0144	0.0611	330	18.0	4.8
1,2,4,-trichlorobenzene	0.00549	0.0193	1050	20.2	5.8
1,2,4,5-tetrachlorobenzene	0.00175	0.0979	6610	647	11.6
1,1,2-trichloroethane	0.368	0.0676	11.2	0.763	4.1
1,1,2,2,-tetrachloroethane	0.115	0.123	107	13.2	12.3
trichloroethylene	0.222	0.398	26.3	10.5	5.9
tetrachloroethylene	0.0524	0.0454	251	11.4	13.2
2,4,6-trichlorophenol	0.0112	0.106	87	17.5	0.98
2,3,5,6-tetrachlorophenol	0.00519	0.0774	141	10.1	0.73
Pentachlorophenol	0.000766	0.0396	216	8.55	0.17

* Values calculated from as outlined in text.

The chlorophenols represent a different problem due to ionization. There are methods to correct for this (McCarty, 1990), unfortunately there is not sufficient observed residue data to confirm the best method. In this case the American flagfish data set included measured bioconcentration data and, when used in conjunction with the matched toxicity data represents the best data currently available. This toxicity and bioconcentration data were used to estimate k1 and the critical body residue. The estimated critical body residues for the chlorophenols generally fall outside the range estimated for narcotics, with pentachlorophenol, a specific toxicant (metabolic uncoupler), exhibiting the lowest residue.

Modelling Mixtures

The next task is the modelling mixtures. The essence of the approach is to model the contribution of each component independently through time and sum the results to obtain the mixture effect. This is done with the 1CFOK equation presented earlier. An example of the application to a binary mixture of chemicals A and B is presented below. The equations can be expanded to examine mixtures of more than two components. Where Cf is the body residue in the fish, Cw is the toxicant concentration in the water, BCF is the bioconcentration factor, k2 is the elimination rate constant, and t is time, the contribution of each chemical to the residue is:

$$Cf_A+Cf_A = BCF_A*Cw_A*(1-e^{-k2_A*t}) + BCF_B*Cw_B*(1-e^{-k2_B*t})$$

Dividing both sides of the equation by (Cw_A + Cw_B) and defining $f_A = Cw_A / (Cw_A + Cw_B)$ and $f_B = Cw_B / (Cw_A + Cw_B)$ produces:

$$\frac{Cf_A+Cf_B}{Cw_A+Cw_b} = BCF_A*f_A*(1-e^{-k2_A*t}) + BCF_B*f_B*(1-e^{-k2_B*t})$$

This assumes residue additivity and that the threshold mixture LC50 is equal to the sum of the exposure water concentrations. If the mixture critical body residue (Cf_{AR} + Cf_{BR}) is defined as Cf_{MR} and the mixture LC50 (Cw_A + Cw_B) is defined as $LC50_M$, then the equation to estimate mixture residues from LC50s and mixture LC50s from mixture residues is, respectively:

$$\frac{1}{Cf_{MR}} = \frac{BCF_A}{LC50_M} \bullet f_A \bullet (1-e^{-k2_A \bullet t}) + \frac{BCF_B}{LC50_M} \bullet f_B \bullet (1-e^{-k2_B \bullet t})$$

$$\frac{1}{LC50_M} = \frac{BCF_A}{Cf_{MR}} \bullet f_A \bullet (1-e^{-k2_A \bullet t}) + \frac{BCF_B}{Cf_{MR}} \bullet f_B \bullet (1-e^{-k2_B \bullet t})$$

The results of the first modelling exercise are presented in Table 2. In this case the objective was to take the water concentrations used in the mixture exposures and model a critical body residue estimate for each mixture. The actual exposure water levels for each chemical in each mixture were calculated from the respective single exposure threshold LC50 and the proportion of the LC50 that was used in the mixture. The fraction of the total mixture water concentration that each comprises (f_A etc.) is presented in Table 2, in brackets, as a proportion of the total molar exposure water concentration.

As can be seen in Table 2 the modelled mixture residues for the narcotics are in good agreement with what was expected. All estimated mixture residues are within the estimated adjusted critical body residue range of 4.4 to 16.2 mmol/L or kg of fish. Although the likelihood of more than one mode of action and the uncertainty caused by ionization make the estimation more speculative for the chlorophenols, the estimated residue does occur, as expected, below the range for simple narcotics.

Table 2: Modelling the Exposure of American Flagfish to Some Organic Chemicals Mixtures Based on Data Obtained with Single Chemical Exposures

Chemical	Threshold LC50 mmol/L	Proportion of 96-h LC50 in Mixture	Mixture Exposure mmol/L (Proportion)[1]		Modelled Residue mmol/L	Estimated Total Residue mmol/L
1,4,-dichlorobenzene	0.0144	0.63	0.00907	(0.865)	2.67	
1,2,4,-trichlorobenzene	0.00549	0.28	0.00154	(0.12)	1.38	
1,2,4,5-tetrachlorobenzene	0.00175	0.09	0.0000158	(0.015)	1.04	
						5.09
1,1,2-trichloroethane	0.368	0.79	0.291	(0.92)	3.26	
1,1,2,2,-tetrachloroethane	0.115	0.21	0.0242	(0.08)	2.59	
						5.85
trichloroethylene	0.222	0.70	0.155	(0.91)	4.10	
tetrachloroethylene	0.0524	0.30	0.0157	(0.09)	3.95	
						8.05
2,4,6-trichlorophenol	0.0112	0.68	0.00762	(0.837)	1.26	
2,3,5,6-tetrachlorophenol	0.00519	0.28	0.00145	(0.16)	0.19	
Pentachlorophenol	0.000766	0.03	0.0000306	(0.003)	0.0065	
						1.46

1. The exposure concentration in mmol/L represents the actual exposure concentration of each isomer in the mixture while the proportion represents the same information in a toxic unit scale.

The results of the second modelling exercise are presented in Figures 1 to 4. In these figures the mean and 95% confidence intervals of the mean of an actual mixture bioassay are presented for various exposure times. The mean and expected range (8.6, 4.4-16.2 mmol/L or kg of fish) of the critical body residue for narcotics (Cf_R), along with the respective component proportional exposure fractions and rate constants, were used in a 1CFOK model to determine exposure water concentration necessary to generate the body residues contributed by each chemical and, ultimately, to estimate a mixture LC50 that would have generated these total mixture residues.

Chlorobenzenes

$$\frac{1}{LC50_M} = \frac{330}{Cf_R} * 0.865 * (1-e^{-0.0611*t}) + \frac{1050}{Cf_R} * 0.12 * (1-e^{-0.0193*t}) + \frac{6610}{Cf_R} * 0.015 * (1-e^{-0.0979*t})$$

Chloroethanes

$$\frac{1}{LC50_M} = \frac{11.2}{Cf_R} * 0.92 * (1-e^{-0.0676*t}) + \frac{107}{Cf_R} * 0.08 * (1-e^{-0.123*t})$$

Chloroethylenes

$$\frac{1}{LC50_M} = \frac{26.3}{Cf_R} * 0.91 * (1-e^{-0.398*t}) + \frac{251}{Cf_R} * 0.09 * (1-e^{-0.0454*t})$$

In all three cases the independently observed mixture toxicity data fell within the range predicted by the model. In each case the time course of the mean estimate was somewhat below the time course of the observed data, but the shape of the toxicity curve was similar to that of the observed data. Trial and error fitting of residues produced the optimal fit indicated in Figures 1 to 3. The critical residues employed in the optimal fit were 5.0, 5.9, and 5.8 mmol/L, respectively. This suggests that the mean critical residue for these chemicals may have actually been slightly lower that the fathead minnow estimates adjusted for differences in lipid content. As initial modelling study these results can be considered good.

The chlorophenols were a problem, both due to ionization and likelihood of different modes of action. In the interests of examining mixture toxicity with these chemicals a modified approach was used. Instead of using the adjusted narcotic critical body residues from the fathead minnow data, the critical body residues estimated for each chemical and this species in the first stage modelling were used; that is, 0.98, 0.73, 0.17 mmol/l, respectively (See Table 1). To obtain some indication of the sensitivity of the analysis to variations in body residue, a range was estimated by arbitrarily assigning a low residue value of ½ and a high residue value of twice, the each of the original estimates. The model equation is:

Chlorophenols

$$\frac{1}{LC50_M} = \frac{87}{0.98} * 0.837 * (1-e^{-0.106*t}) + \frac{141}{0.73} * 0.16 * (1-e^{-0.0774*t}) + \frac{216}{0.17} * 0.003 * (1-e^{-0.0396*t})$$

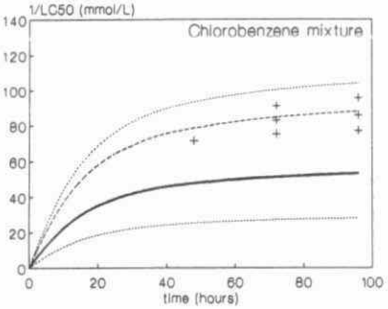


Figure 1: Mean and Range of 1CFOK Mixture Model Compared with Observed Data For American Flagfish Exposed to a Chlorobenzene Mixture

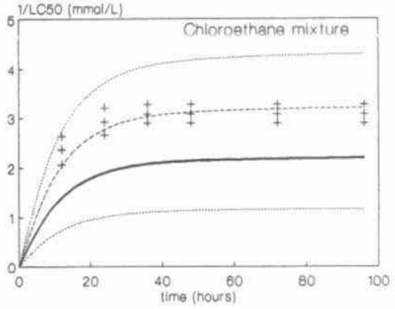


Figure 2: Mean and Range of a 1CFOK Mixture Model Compared With Observed Data for American Flagfish Exposed to a Chloroethane Mixture

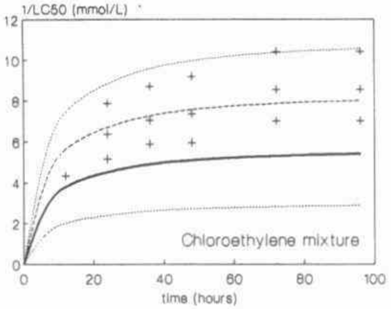


Figure 3: Mean and Range of a 1CFOK Mixture Model Compared to Observed Data for American Flagfish Exposed to a Chloroethylene Mixture

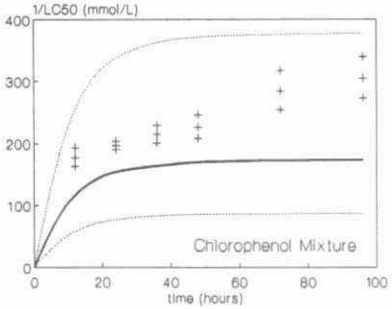


Figure 4: Mean and Range of a 1CFOK Mixture Model Compared to Observed Data For American Flagfish Exposed to a Chlorophenol Mixture

Crosses represent observed LC50 data and 95% CI. Lines represent modelled LC50 estimates based on critical body residue estimates of 8.6 mmol/L of fish (solid line), 4.4 and 16.2 mmol/L (dotted lines), and optimal fit (dashed line).

As can be seen in Figure 4, the modelled data range for the chlorophenols includes the observed mixture toxicity data. The process has generated a description of the time course of an independently measured mixture toxicity bioassay, based on a mixture model employing single exposure data for each of the components, which is in reasonable agreement with the observed data.

Discussion

As noted at the beginning, success in this modelling exercise was to be determined on the basis of whether modelled molar LC50s for mixtures were in reasonable agreement independently obtained toxicity data. In the first exercise, presented in Table 2, the estimated critical body residues generated by the mixture model approach all fell in the expected range, 4.4-16.2 mmol/kg. Although less confidence is placed in the modelling with chlorophenols, due to the variability introduced by ionization and the probable presence of more than one mode of toxic action, the estimated critical body residue was below the lower limit of the expected narcotic range, as expected.

In the results of the modelling exercise presented in Figures 1 to 4, it appears that data obtained from single chemical toxicity testing results (k2 and threshold LC50), as well as data estimated independently from these toxicity bioassays (BCF and critical molar residue), can be successfully combined with the 1CFOK modelling procedure to reasonably reproduce the time-LC50 data observed in bioassays with certain mixtures of organic chemicals.

Both the threshold LC50 achieved and prediction of the intermediated LC50 observations provide confirmation of the success of the modelling exercise. The former is obvious but the latter is less so. The modelling process has synthesized 1CFOK kinetics for the mixture. In a 1CFOK model the elimination rate constant, k2, determines the shape of the curve as it approaches steady-state, while the uptake rate constant, k1, determines the magnitude of the bioconcentration above (or below) the exposure water concentration. Since BCF = k1/k2, it is possible to have a BCF which produces model data which agree with observations at threshold but does not agree with the time course of achieving threshold. Thus, if the modelled time-course is similar to the observed data it represents additional evidence supporting the validity of the model in interpreting the observations. Of course, agreement of both the modelled threshold and the time course do not guarantee validity for the model; this would require independent confirmation by means of measured kinetics and body residues. Nevertheless, the models of each of the three mixtures of narcotics appear to provide reasonable agreement with both the time course and the ultimate thresholds in the observed bioassays. The chlorophenol model can be considered reasonably successful despite the problems associated with determination of the critical body residues. The fit of the model to the data is aided by the fact that, in all cases, one chemical in the mixture dominates (63-79%). Thus, much of the model prediction of the mixture toxicity may be based on the ability to model the dominant chemical, although Hermens *et al.* (1984a&b) found that mixture toxicity of narcotic chemicals appeared to be simply additive over a wide range of mixture ratios.

It should be noted that the toxic unit approach can be used to describe the time course of mixture toxicity without knowing the critical body residue. In fact, the modelling procedures reported above are essentially identical as both employ 1CFOK assumptions and manipulate the same equations. However, the difference is that the modelling carried out above focuses on the importance of critical body residue. Thus, it can be used to both describe and interpret bioassay data, while a kinetics-based toxic unit approach without residue information is restricted, with some limitations, to describing the data. As noted in earlier chapters, the difficulties of attempting to interpret and employ toxicity bioassay data without knowledge of the critical body residue has been described by Mancini (1983) and others. Hence, the determination of threshold in a mixture is equally as important for the toxicological interpretation of the data as it is in the case of single chemical toxicity bioassays, and all of the caveats discussed earlier apply, as again the exposure water concentration(s) are being used as a surrogate for the critical body residue(s). Thus, modelling carried out above can be viewed as a logical extension of the basic toxic unit approach, which is more useful in its examination of mixture toxicity over a time-concentration continuum and more informative due to its focus on toxicant potency based on critical body residues.

This feasibility study suggests that the combination of the critical body residue concept and a simple 1CFOK model of toxicant accumulation can be used to model mixtures of chemicals with a similar mode of toxic action. Residue-based 1CFOK modelling of mixtures provides the same advantages as found in single chemical exposures. Although both the steady-state and the time course of reaching that steady-state can be described by models without the knowledge of the critical body residue (i.e. the toxic unit method can be used to describe the time course of mixture toxicity), it is not possible to determine the toxicological significance - potency of the toxicant in the organism - without that knowledge.

Conclusions

1. A one-compartment, first-order kinetics model of accumulation combined with the critical body residue concept, as defined for neutral, narcotic organics, adequately explains the observed time-LC50 data for independently observed bioassays of mixtures of chlorobenzenes, chloroethanes and chloroethylenes.

2. A similar modelling exercise for a mixture of chlorinated phenols, although more restricted due to the nature of the available data, also adequately explained the observed time-LC50 results for a chlorophenol mixture.

3. The advantages of a residue-based, toxicokinetic model approach to mixture toxicity over the "toxic unit" method include: the methodology is similar to that used for single chemical toxicity, the toxicant kinetics are a fundamental component, and the association of biological responses with molar toxicant residues in the organism focuses attention on the more toxicologically relevant site(s) of toxic action in the organism, rather than the exposure concentrations.

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VERIFICATION OF A BIOCONCENTRATION-BASED MODEL FOR PREDICTING PULSE-EXPOSURE TOXICITY OF ORGANIC CONTAMINANTS TO FISH.

B.E. Hickie and D.G. Dixon

Department of Biology, University of Waterloo,
Waterloo, Ontario, Canada, N2L 3G1.

INTRODUCTION

In standard laboratory toxicity tests organisms are continuously exposed to constant toxicant concentrations. In these tests, organisms generally come to a steady-state toxicant body concentration, allowing the aqueous exposure concentration to be used as a surrogate for the internal dose in forming a dose-response relationship. Water quality objectives are developed from no-effect exposure concentrations derived from such tests, and are then applied in field situations where exposures are rarely constant due to such factors as: varying rates of input, dilution, and degradation. The U.S. EPA (1979) attempted to deal with pulse and fluctuating exposures by proposing a two-number criteria (TNC), specifying a 24-h average and a peak concentration not to be exceeded. The two concentrations were based on the no-effect level and the LC50. Several studies (Ingersoll and Winner, 1982; Seim *et al.*, 1984) have shown that the proposed TNC formula did not consistently protect life. This was likely due to exposure being an inadequate dose surrogate for exposures where steady-state is not achieved.

Several studies (Hodson *et al.*, 1983; Mancini, 1983; Wang and Hanson, 1985) have used simple toxicokinetic models to estimate the dose accumulated in time-varying exposures, thus allowing for a direct examination of the dose-response relationship. We have developed a bioconcentration-based model (PULSETOX) to track the dose an organism receives under cyclic or randomly fluctuating exposure conditions. The model is an adaptation of the simple, one-comparment, first-order toxicokinetic model (1CFOK) described by Spacie and Hamelink (1982) where:

$$C_f = C_w \frac{k_1}{k_2} \left(1 - e^{-k_2 \cdot t}\right) \qquad (1)$$

C_f = toxicant concentration in fish at time t.
C_w = toxicant concentration in water.
k_1 = uptake rate constant.
k_2 = clearance rate constant.
k_1/k_2 = bioconcentration factor (BCF).
t = time.

Numerical integration techniques are used to generate a time-course output of the exposure regime and accumulated dose (Figure 1), as well as a summary of the exposure including: the maximum values of Cw and Cf achieved, and the area under the curve for exposure and dose. Since the model has input variables describing the chemical (Kow, BCF, k_2), the organism (weight, lipid content), and the exposure (concentration, duration, frequency), it forms a framework for hypothesis testing.

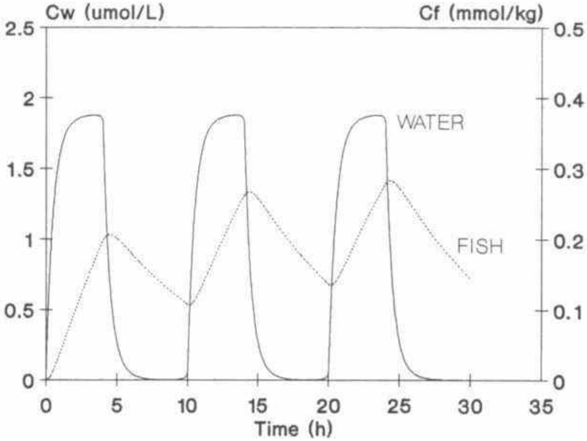

Figure 1. Example of graphical output of time-course for Cw and Cf from PULSETOX model.

Since the organism is considered as a single compartment in the model, prediction of effects are based on the whole body toxicant concentration. For lethality, predictions of effects are based on the maximum dose accumulated, with a lethal effect resulting from the organism reaching a certain critical dose (Cfr) which is characteristic of the toxicants mode of action. For narcotic organic chemicals, which include the majority of industrial organic compounds (Veith *et al*., 1983), the median lethal Cfr value is in the range of 3 to 6 mmol/kg. For pentachlorophenol (PCP), which acts as a metabolic uncoupler, the lethal Cfr measured in fathead minnow was 0.28 mmol/kg (Spehar *et al*., 1985). Since the value of Cfr for a chemical can be estimated as the product of the threshold LC50 and the BCF, the Cfr may also be considered as an estimate of the LD50 (McCarty, 1990). The model may also be used in a backward fashion, and work from the Cfr to predict the pulse LC50 for any defined exposure regime.

This paper reports on the initial testing of the PULSETOX model with a set of 26 pulse-exposure lethality tests of PCP to larval fathead minnow (*Pimephales promelas*). The working hypothesis for the model is that the pulse LC50 (median lethal exposure regime) defines the exposure required for an organism to accumulate a dose equivalent to the lethal Cfr or LD50. Also included in the study is direct verification of the lethal Cfr value for PCP.

MATERIALS AND METHODS

A set of continuous and pulse-exposure lethality tests for PCP were conducted with larval fathead minnow (48 to 72-h post hatch) in a flow-through exposure system. Toxicant delivery to the exposure system was controlled with an automated multi-channel peristaltic pump. A continuous exposure test was run to define the threshold LC50 and toxicity curve. A total of 26 pulse-exposure lethality tests were conducted including seven single-pulse tests ranging from 2-h to 48-h, and 19 multiple pulse tests. Multiple exposures were simple repeating cycles, with each cycle consisting of a pulse and an interval prior to the next cycle. For example, Figure 1 shows the form of the exposure for three pulses, four-hours long with a six-hour interval. Each test consisted of five exposure levels plus a control, with 15 to 20 larvae used per level. All tests were run for 144-h to allow for observation of post-exposure mortalities.

Exposure chambers were 6 L glass aquaria which received 0.2 L water/min, giving a 95% molecular replacement time of 2 h. The resulting form of individual pulses were similar to those shown in Figure 1. Exposure conditions for all tests were: temperature, 25±0.5°C; pH, 7.9 to 8.1; total hardness, 275±5 mg/L as $CaCO_3$; alkalinity, 237±3 mg/L as $CaCO_3$; dissolved oxygen, 7.5±0.2 mg/L. Aqueous toxicant concentrations were measured daily during the continuous-exposure test, and at the end of each pulse to define the peak exposure concentrations achieved. Observations for mortalities in the continuous-exposure test were made at 1, 2, 4, 8, 16, and 24-h, and at least daily thereafter. Observations during the pulse tests followed a similar pattern but included at least one observation per pulse cycle.

Median lethal concentrations (LC50) were calculated by the trimmed Spearman-Karber method (Hamilton *et al*., 1977) using measured toxicant concentrations. For the pulse-exposure tests, LC50 calculations were based on the mean peak aqueous concentrations for each exposure regime. Expressing the pulse-LC50s in terms of peak exposure concentration allows the median lethal exposure regime to be reconstucted easily in modelling. The PULSETOX model was then used to estimate the maximum PCP residue accumulated by fish in the median lethal exposure regimes. The toxicokinetic parameters employed in modelling were determined in two ways: from [^{14}C]PCP accumulation studies; and by fitting the 1CFOK model to the toxicity curve derived from the continuous exposure test following the method described by McCarty *et al*. (1989). The [^{14}C]PCP accumulation study yielded the following kinetics estimates: BCF, 286; k_1, 76.17 h^{-1}; k_2, 0.266 h^{-1}. The toxicity-derived kinetics estimation method yields an estimate of the threshold LC50 and the k_2 which was 0.212 h^{-1}. This value is similar to the ^{14}C-derived estimate.

Residue analysis was conducted to verify the value of the lethal dose (Cfr) for PCP. This was done with larger fathead minnows (0.2 to 1.6 g) which were drawn from continuous exposure lethality tests which were conducted under similar conditions to those reported here. Analysis included fish that died during the tests, as well as fish from the highest exposure concentrations with survivors. This was done to determine whether whole body toxicant residues could delineate between live and dead fish and fit a classic dose-response model. Whole fish were digested in concentrated HCl, followed by extraction of PCP with hexane. The hexane extract was eluted through an Na_2SO_4 column, concentrated by rotary-evaporation, and then eluted through a silica-sulfuric acid (40% by weight) column to remove lipid. The PCP was then extracted into 5.0 mL of 0.1 M NaOH which was passed through a 0.45 µm filter prior to analysis. PCP was measured using HPLC with UV detector (235 nm) and a C-8 reverse phase column. The mobile phase was a 75:25 methanol:water mixture with 1% v/v acetic acid. The average recovery of PCP was 92.5% (±3.7%).

RESULTS AND DISCUSSION

The mean whole body PCP residue in dead fish was 0.30 mmol/kg (SD±0.02, C.V.=6.6%, n=11) and was equivalent to that reported by Spehar *et al.* (1985) (Figure 2). This measure of Cfr is a stable estimate of PCP toxicity to fish since it was independent of time to death, exposure concentration, and fish weight (multiple regression p = 0.35). The PCP residues in fish surviving 144-h at an exposure concentration equivalent to 76% of the LC50 often exceeded those measured in dead fish, with levels tending to be higher in larger fish. This appears to contradict the classic dose-response relationship, and demonstrates that the whole body toxicant residue is not an ideal surrogate for the dose at the site(s) of action. Storage or partitioning of much of the accumulated PCP away from sites of activity is the most likely explanation for this. A better understanding of this phenomen is required if whole body toxicant residues are to be related to effects.

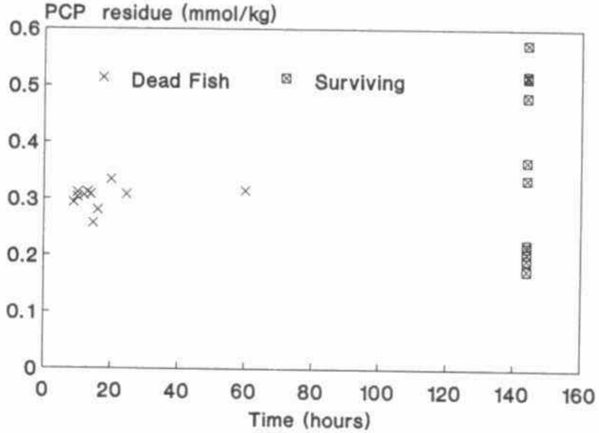

Figure 2. Measured whole body PCP residues in dead fish, and in fish suviving exposure equivalent to 76% of the LC50 for 144-h.

The continuous exposure threshold LC50 (95% C.L.) for larval fathead minnow was 0.89 μmol PCP/L (0.82-0.99). Since the lethal threshold was reached by 24-h, pulse-exposure durations less than this were emphasized in the data set. The set of pulse LC50 values are reported in Table 1. The single pulse-LC50s decreased with increasing exposure duration and form a curve similar to an ideal toxicity curve. For multiple pulses, the exposure and interval duration, as well as the number of pulses affected pulse LC50 values.

The calculated area under the exposure curve associated with each LC50 are also given in Table 1. They are similar to the average exposure concentration, and are useful since they summarize complex exposures into a single value. The pulse LC50 values do not relate well with the exposure area (Figure 3), or with other methods of expressing exposure. This demonstrates that exposure, expressed by any means, is an inadequate surrogate for dose when a steady-state is not reached.

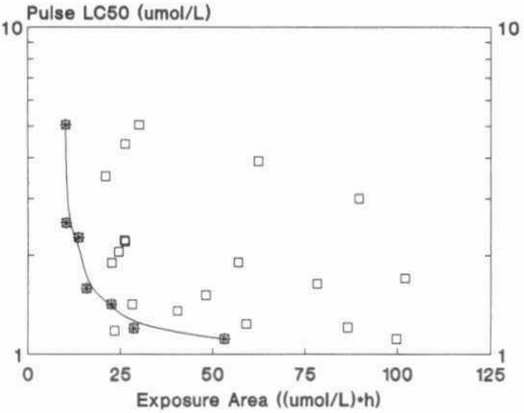

Figure 3. Pulse LC50 values, expressed as mean peak concentrations plotted against area under exposure curve. The curve joins single pulse LC50s.

The PULSETOX model estimated Cfr values derived using ^{14}C and toxicity-based toxicokinetic parameters are given in Table 1, and shown in Figures 4 and 5 respectively. Using the ^{14}C-derived kinetics, the mean estimated Cfr value was 0.38 mmol/kg fish (SD = 0.07; CV = 18.4%). For the toxicity-derived kinetics, the mean estimated Cfr value was 0.36 mmol/kg fish (SD = 0.04; CV = 18.4%). These values were nominally higher, but not significantly different than the measured Cfr value.

Table 1. Pulse LC50, based on peak water concentration, model-calculated area under curve for LC50 exposure level, and model-estimated Cfr using ^{14}C and toxicity-based kinetics estimates for PCP pulse lethality data set. Each pulse exposure test is defined on the basis of pulse duration, interval between pulses, and number of pulse exposures.

Pulse Definition			Pulse LC50	Summed LC50	Model Estimated Cfr	
duration (h)	interval (h)	number	(95% C.L.) (µmol/L)	Exposure Area ((µmol/L)·h)	(mmol/kg fish) ^{14}C	Toxicity
2	-	1	5.04 (4.24-5.98)	10.02	0.52	0.45
	6	3	3.51 (3.11-3.95)	20.95	0.42	0.39
	6	15	3.00 (2.63-3.41)	89.55	0.36	0.34
	14	3	4.40 (4.13-4.70)	26.31	0.46	0.41
	14	8	3.91 (3.16-4.84)	62.33	0.41	0.36
	22	3	5.04 (4.24-5.98)	30.11	0.52	0.45
4	-	1	2.52 (2.35-2.71)	10.03	0.44	0.38
	6	3	1.89 (1.81-1.99)	22.63	0.36	0.33
	6	12	1.64 (1.45-1.85)	78.31	0.31	0.29
	16	3	2.05 (1.88-2.24)	24.52	.036	0.32
	16	8	1.51 (1.31-1.74)	48.15	0.27	0.24
6	-	1	2.27 (2.08-2.50)	13.57	0.50	0.45
	6	2	2.18 (1.86-2.57)	26.08	0.51	0.47
	6	10	1.70 (1.39-2.08)	101.69	0.39	0.37
	18	2	2.20 (1.89-2.56)	26.36	0.49	0.43
	18	5	1.91 (1.53-2.38)	56.92	0.42	0.38
10	-	1	1.58 (1.47-1.71)	15.74	0.41	0.39
	6	2	1.18 (1.08-1.29)	23.64	0.31	0.30
	6	9	1.11 (1.02-1.22)	99.66	0.30	0.29
	22	2	1.42 (1.34-1.50)	28.21	0.37	0.35
	22	3	1.35 (1.23-1.48)	40.41	0.35	0.33
16	-	1	1.42 (1.25-1.61)	22.56	0.40	0.39
24	-	1	1.20 (1.05-1.37)	28.63	0.34	0.34
	24	2	1.23 (1.06-1.45)	59.06	0.35	0.34
	24	3	1.21 (1.08-1.36)	86.47	0.34	0.34
48	-	1	1.11 (0.99-1.25)	53.16	0.32	0.32

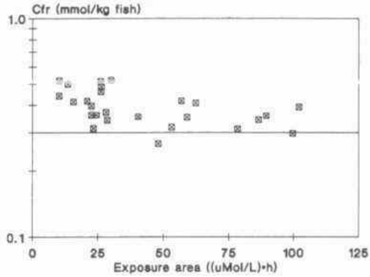

Figure 4. PULSETOX-estimated Cfr values for PCP pulse-exposure data set using ^{14}C-derived kinetics parameters. Mean measured Cfr is shown as horizontal line (Cfr = 0.30 mmol/kg).

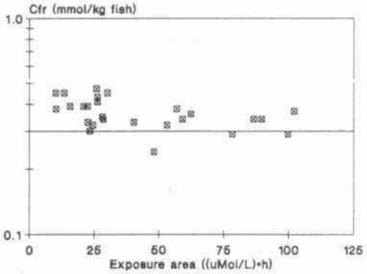

Figure 5. PULSETOX-estimated Cfr values for PCP pulse-exposure data set using toxicity-derived kinetics parameters. Mean measured Cfr is shown as horizontal line (Cfr = 0.30 mmol/kg).

Figures 4 and 5 show that the model tended to overestimate the Cfr values for the exposures with a lower exposure area, or short duration exposures. This overshoot effect could arise if there were a lag in organism response after accumulating the lethal dose. This is also reflected in linear regressions between observed and predicted pulse LC50s since the slopes exceed unity.

For ^{14}C-derived kinetics:

$$\text{pred. LC50} = 1.79\ (\text{obs. LC50}) - 0.86 \quad (p < 0.001,\ r^2 = 0.965,\ n = 26)$$

For toxicity-derived kinetics:

$$\text{pred. LC50} = 1.53\ (\text{obs. LC50}) - 0.58 \quad (p < 0.001,\ r^2 = 0.967,\ n = 26)$$

Based on the lower slope, the toxicity-derived kinetics were better in predicting pulse LC50 values. This may be due to the incorporation of both accumulation and response information into the k_2 estimated by this means, thus accounting for some part of the response lag. Further improvement on predictability may be achieved by using the k_2 estimated from a toxicity curve constructed from the set of single pulse LC50 tests. This resulted in a lower k_2 estimate of 0.122 h^{-1}. Using this value in the PULSETOX model yielded a mean estimated Cfr value of 0.30 mmol/kg fish (SD = 0.04; CV = 13.5%), equivalent to the measured value. Using the pulse-estimated kinetics, the model demonstrated an excellent capability to predict pulse LC50 as shown by the following regression:

$$\text{pred. LC50} = 0.99\ (\text{obs. LC50}) - 0.06 \quad (p < 0.001,\ r^2 = 0.940,\ n = 19)$$

The LC50 values for single pulse-exposures were exluded from this regression to avoid pseudo-replication. While predictability was dependent on the kinetics used, the model showed a robust ability to account for the variability in pulse LC50 values, as shown by the high r^2 for each regression.

Overall, the PULSETOX model provides a useful deterministic approach for predicting effects of time-varying exposures. This study clearly shows that toxicokinetics forms the critical link between exposure and dose necessary for evaluating toxicity resulting from non-steady-state exposures. The critical body residue concept employed here should also be applicable to other complex exposure problems such as mixtures and sediments.

Acknowledgement: Dr. D. Mackay, and Dr. L.S. McCarty provided valuable assistance in developing the PULSETOX model.

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MAPPING LAKE WATER QUALITY CHARACTERISTICS USING LANDSAT THEMATIC MAPPER DATA

J. Roger Pitblado, T.L.M. Jetty,
R.L. O'Daiskey, and Dale A. Dempsey
Geography Department, Laurentian University
Sudbury, Ontario P3E 2C6

INTRODUCTION

This report provides a summary of some of the most recent and planned activities associated with our efforts to derive relationships between lake water quality and satellite reflectance data (R.A.C. Project No. 354G). The study area of greatest emphasis has been in eastern Northern Ontario, defined approximately: from Highway 11 (Hearst to Cochrane) south to the North Channel of Georgian Bay; and from the eastern shores of Lake Superior to the vicinity of North Bay. A second area of interest has been the Quetico region of Northwestern Ontario; and a final region, not yet sampled, the area south of Lake Nipissing which we refer to as the Algonquin/Dorset area.

Over the past three years, through the annual M.O.E. Technology Transfer Conference, we have outlined various strategies for describing the relationships between and predicting selected water parameters (notably Secchi disc depth and dissolved organic carbon concentrations; discrimination between acidic and non-acidic lakes; and discrimination between lake groups of significant trophic status differences) using reflectance data recorded by a number of remote sensors. The major sensor, given that our prime task was to examine satellite data, has been the Thematic Mapper (TM) on board Landsats 4 and 5.

Those efforts are continuing, with a number of planned innovations to the overall water quality-reflectance research thrust. In addition, however, we are now faced with providing a means to illustrate those derived water quality-reflectance relationships for a very large area of the Province; and also to provide an efficient means of updating our databases with new information derived both or either from *in situ* lake water samples and satellite reflectance data. Thus, a significant portion of our attention at present has turned to the problems of computer mapping and relational database management systems (RDBMS). The computer mapping/RDBMS programme is being facilitated by the integration of remote sensing and geographical information systems (GIS) technologies.

WATER QUALITY - REFLECTANCE ASSESSMENTS

Acquisition of Spectral Reflectance Data for Northeastern Ontario Lakes

Lakes, lakes, lakes! It has been said that there are 250,000 lakes in the Province of Ontario. We believe it, and then some! For the better part of the Summer of 1990, we have been gathering Landsat TM spectral data for all lakes of "sufficient size" in the area described above as our main study region. At this point close to 85% of the study area has been surveyed.

The criteria that we are using as "sufficient size" are that a lake must contain approximately 10 Landsat picture elements or pixels (4-5 ha) and there must be more than one pixel on either side of the lake centroid. We are trying to avoid 'mixels' which are combinations of water-terrain reflectance and to avoid bottom effects as much as possible. While the final statistics have yet to be computed, most of the sampled lakes are 10 ha in size or greater. Many lakes that are 10 ha or smaller (and even some that are larger) have not been selected because they are too long and thin to meet the criteria above.

This sampling protocol should significantly add to the database of the Ontario Ministry of the Environment, especially in the proportion of smaller Ontario lakes. Given the difficulties of providing provincial estimates of lake acidification (Neary et al., 1990), we are confident that these data will be beneficial for lake water quality assessments and monitoring.

Once all the candidate lakes have been selected, TM reflectance and area statistics will be computed and then associated (using multiple regression and multivariate discriminant analyses) with the limited water quality characteristics that have been provided from MOE and MNR lake inventories. Based on the successful derivations of associations between lake water quality and Landsat TM reported in the past (Pitblado 1987; Pitblado et al. 1987; Pitblado 1988; Pitblado and Dempsey 1989), we do not anticipate difficulties here.

Acquisition of Spectral Reflectance Data for Algonquin/Dorset Area Lakes

Following the same protocol as outlined above, Landsat TM reflectance data for lakes located south of Lake Nipissing are to be acquired. For that area we have one mid-summer digital image and a late-spring image. All of the previous work that has been undertaken during this research project has focused on the use of mid-summer imagery -- at the same time as or very close to the dates when lake water quality samples have been gathered. If the late-spring image is employed, it will be our first temporal assessment of associations between lake reflectance and lake water quality.

Bowland Lake

The majority of water quality studies based on the use of remotely sensed data (our own and elsewhere) has focused spatial parameters. That is, given satellite data (and in some instances other sensors) of the same or similar date, researchers have identified between-lake or within-lake differences. Both qualitative and quantitative assessments of differences are now fairly common. Very few temporal assessments have been undertaken (Pitblado 1990). And to our knowledge, no temporal assessments using satellite data have been attempted for an acidic lake that has been subjected to an acid neutralizing programme.

Our final task in this part of the research programme will be to examine the temporal water quality-spectral characteristics of Boland Lake (47°05'N, 80°50'W). Ten dates of imagery (from 1973 to 1986) are available for this assessment. Theoretically these dates nicely span the before-during-after time period with respect to the neutralization of the lake in August of 1983. Some of these images may have to be eliminated from the analysis because (at least as viewed from poor quality microfiche) there is some cloud or haze above or nearby Bowland Lake.

This will be an extremely interesting experiment, first because of the water quality changes known to have occurred over this time period (Keller et al. 1990; Molot et al. 1990). And second, because the images are derived from four different Landsat satellites using two different sensors (the MSS, multispectral scanner of Landsats 1,2,3 and the TM, thematic mapper of Landsat 5).

Modelling

The work outlined above and described in more detail elsewhere clearly identifies that relationships exist between water quality parameters (or groups of parameters) and water colour, and that satellite sensors can measure water colour with sufficient sensitivity to monitor changes in water quality. A complementary, and necessary, next step is to develop a fundamental understanding of why these relationships exist and what controls them. Field investigations were recently initiated for this task by Ann Gallie (personal communication, Laurentian University) which will further our ability to interpret water colour and water clarity in terms of water quality and to understand the conditions under which empirical relationships will hold (see also, Pitblado and Gallie 1990). Gallie's work focuses on the development of a theoretical optical water-quality model for Northern Ontario. The model is based on the reflectance equations of Gordon et al. (1975) relating reflectance to the inherent optical properties of the water body as well as accounting for atmospheric and water surface effects (Gallie, 1990).

REMOTE SENSING - GIS INTEGRATION

As suggested above, hundreds of lakes in Northeastern Ontario are being examined through this research project. The data associated with each lake consists of: the mean spectral characteristics for each of seven Landsat TM spectral bands for ALL of the sampled lakes; the mean spectral characteristics for each of four Landsat MSS spectral bands for 90 lakes in the immediate Sudbury area; the mean spectral characteristics for each of eleven airborne Daedulus spectral bands for 20 lakes north of Lake Wanapitei; and up to 30 water quality parameters (e.g. pH, DOC, Secchi disc depth, Ca, Mg, chlorophyll a, etc.) for a relatively small fraction of those lakes sampled using the satellite imagery. The latter data were derived from field studies, undertaken by the senior author, the Ontario Ministry of the Environment, or the Ontario Ministry of Natural Resources. The handling of this spatially and temporally diffuse data has lead us to employ the techniques/technology of geographical information systems (GIS).

Geographical information systems are fundamentally collections of computer hardware and software modules designed for the capture, storage, display, analysis, and output of spatially related data. Goodchild and Brusegard (1989) have identified 65 generic GIS functions and the fact that major systems often have over 1000 commands or functions. The function that we are presently grappling with, as we integrate remotely sensed data into a commercial GIS, is image rectification and/or data transfer.

The geometry of Landsat satellite orbits is such that some form of rectification is required for compatibility with a GIS where a reference coordinate system is the foundation of the data base. This coordinate system, given that when working in Ontario and Canada with digital maps from the Ontario Basic Mapping System or the National Topographic System respectively, is the Universal Transverse Mercator (UTM) projection.

Standard procedures exist for the rectification of Landsat imagery to a UTM coordinate system, i.e. to transform image coordinates to ground coordinates. The three most popular procedures are (after Silfer 1988):

a) nearest neighbour - uses the intensity of the closest pixel to assign a value to the output pixel.

b) bilinear interpolation - uses four neighbouring pixel's values and interpolates an output value.

c) cubic convolution - uses sixteen neighbouring pixil's input values to interpolate an output value.

For the analysis of the lakes in Northeastern Ontario, all of these procedures significantly alter the numerical values of reflectance value means in each of the TM or MSS bands. These algorithms were not designed to make the sharp water/not-water distinctions that we require in this study when moving from the raster-based data structure of our imagery to the vector-based data structure of our GIS. Consequently, we have adopted a semi-automated means of transferring imagery data to the GIS environment. It requires that: numerical lake IDs be generated which are the linking-keys between the two systems; lake reflectance means generated in the image analysis environment, i.e. no geometric corrections undertaken for the Landsat data; and then those numerical values transferred to keyed lakes in the vector-GIS environment using a standard input function of the GIS software. The data identifying the lake boundaries in the GIS system are vectors abstracted from OBM or NTS digital files based on the UTM grid system and ranging in scales from 1:20,000 to 1:250,000.

It is well known that the building stage of a GIS is the most time-consuming and laborious/tedious. We are presently going through that stage is building a GIS database for lakes in Northeastern Ontario. Once completed, we are confident that it will be ideal for analyses, mapping and monitoring lake water quality (with or without the aid of a remote sensing component).

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MULTISPECTRAL REMOTE SENSING TECHNIQUES for PAST, PRESENT and FUTURE MAPPING of CHLOROPHYLL

Arunas Kalinauskas *, Moniteq Ltd., 630 Rivermede Rd., Concord, Ontario L4K 2H7, Neil Hutchinson and Bernie Neary, Limnology Section, Dorset Research Centre, Water Resources Branch, Ministry of the Environment, Bellwood Acres Road, P.O. Box 39, Dorset, Ontario POA 1EO.

Extended Abstract

Multispectral remote sensing, both from satellite and aircraft, offers the potential for large scale routine water quality monitoring. Complementary to in-situ techniques, remote sensing provides highly detailed information on the spatial distribution of suspended solids and chlorophyll concentrations.

Satellite remote sensing in the past has been hampered by the lack of spectral resolution. MONITEQ Ltd. has designed and developed an airborne digital imaging system the Fluorescence Line Imager - FLI (also known as Programmable Multispectral Imager - PMI) as a prototype for satellites which will be launched in the late 1990's.

One of the objectives of this project was to make use of the FLI/PMI's high spectral resolution to simulate data from past, present and future satellites. This has been accomplished using FLI/PMI data collected over a portion of the Lake of the Woods, Ontario. Further processing of this dataset has produced a new model for detection and mapping of inland lake surface chlorophyll concentration. The results of this new model have produced an $r2=0.96$ correlation to in-situ water samples collected at the same time as the airborne FLI/PMI data capture.

Through this project the spectral location of freshwater chlorophyll fluorescence line was identified (approximately 705 nm) using the airborne FLI/PMI sensor. Making use of the high spectral resolution we believe that a four channel sensor can be developed to map chlorophyll for Ontario's lakes. A model very similar to the marine chlorophyll Fluorescence Line Hight (FLH) technique developed by Gower and Borstad (several publications) can be applied for a very economical monitoring methodology.

We will further discuss the model optimization used to compute both turbidity and chlorophyll concentrations and identify its potential use with future satellite data.

Another objective of this study was to examine the potential of processing historic satellite (LANDSAT) databases dating back as far as 1972 which can then be reviewed and correlated to changes in water quality and establish trends. The FLI/PMI data was used to simulate the LANDSAT multispectral channels and then processed for chlorophyll and turbidity. These simulated satellite data products were compared to the output from the FLI/PMI model and to the processed results from LANDSAT data (collected the day after FLI/PMI data capture) over the same site. The results of this comparison show that the greater spectral and spatial resolution of the FLI/PMI provides the best product. However, historic satellite data can show general trends in water quality, which can provide hindsight to the resource manager.

REGIONAL ANALYSIS OF LOW FLOW CHARACTERISTICS FOR CENTRAL AND SOUTHEASTERN REGIONS

H. S. Belore, D. F. Ashfield and S. P. Singh
Cumming Cockburn Limited, 145 Sparks Avenue, Willowdale, Ontario, M2H 2S5

ABSTRACT

Low flow statistics for ungauged watersheds are essential for analysing water quality conditions and environmental impacts, etc. This study describes the low flow characteristics of the Central and Southeastern regions defined by the Ontario Ministry of the Environment. Four techniques for estimating low flows, i.e. regression, index, area proration and mapped isolines of unit low flows were developed and compared. Several test stations which were not included in the development of the estimation techniques, were used in evaluating the usefulness and accuracy of the various techniques. The mapped isolines method was found to give the best estimates for estimating low flows of $7Q_2$ and $7Q_{20}$.

INTRODUCTION

Low flow statistics have many uses including analysis of municipal and industrial effluent discharges into streams, instream pollutant analyses, reservoir design for low flow augmentation, environmental approvals, feasibility of small hydro developments, water supply and evaluation for water taking permits, base flow/groundwater recharge and/or contamination analysis, stream fisheries assessments, etc.

The identification of low flow characteristics within a watercourse is most easily accomplished using continuous hydrometric data recorded for the stream. One source of such information describing low flow characteristics are the "Low Flow Characteristics" maps updated by Cumming Cockburn Limited for the Ministry of the Environment (1989). However, the effectiveness of utilizing single station analyses is limited since a hydrometric recording gauge may not be located in the vicinity of the study site.

The most commonly used techniques for estimating low flow characteristics for ungauged watersheds are regression equations based on physiographic and hydrometeorologic basin characteristics, index methods, area proration, and isoline maps.

This project undertook to develop and evaluate these techniques for estimation of low flow statistics for ungauged watersheds.

A REGIONAL PROBABILITY DISTRIBUTION FOR ANNUAL MINIMUM n-DAY AVERAGE DAILY STREAMFLOWS

The development of a generalized method requires selection and use of an appropriate method for analysis of suitable single station measurements of selected low flow characterisics. In addition to a literature review of statistical hydrologic fitting techniques, a previous evaluation of the Biologically Based Low Flow Analysis Technique (Cumming Cockburn, 1990) was also utilized to confirm selection of an appropriate method. On the basis of these comparisons, the Gumbel III distribution was generally applied except for stations with large negative skewness where the 3-Parameter Log Normal distribution was used. Parameter estimation for fitting of distributions proceeded in order of maximum likelihood, smallest observed drought and moments. The results of the extreme value analysis for each station were presented elsewhere (Cumming Cockburn, 1989).

REVIEW OF LOW FLOW ESTIMATION TECHNIQUES

The use of regional regression equations is the most commonly reported technique for estimation of low flow statistics. A summary of various equations developed by others is given in Table 1.

The area proration method is currently being used by many practising hydrologists and by the Ontario Ministry of the Environment for estimation of the low flows and has previously been used by Cumming Cockburn (1990).

The index method has been used by Osborn (1974) and Cumming Cockburn (1990).

Based on the review of literature, it was expected that the regression method would outperform the other techniques.

STUDY REGION

The study was undertaken for the Central and Southeastern regions as defined by the Ministry of Environment (Figure 1). A total of 95 hydrometric stations were identified in the region based upon a screening of data including regulation, outliers, the period of record and other station characteristics. Low flow characteristics for 73 (48 and 25 for the Central and Southeastern regions, respectively) of these stations were analysed to develop the estimation techniques. Twenty-one (12 and 9 for the Central and Southeastern regions, respectively) of those stations remaining were set aside for testing of results. Prediction techniques were developed for each region and for the combined data set.

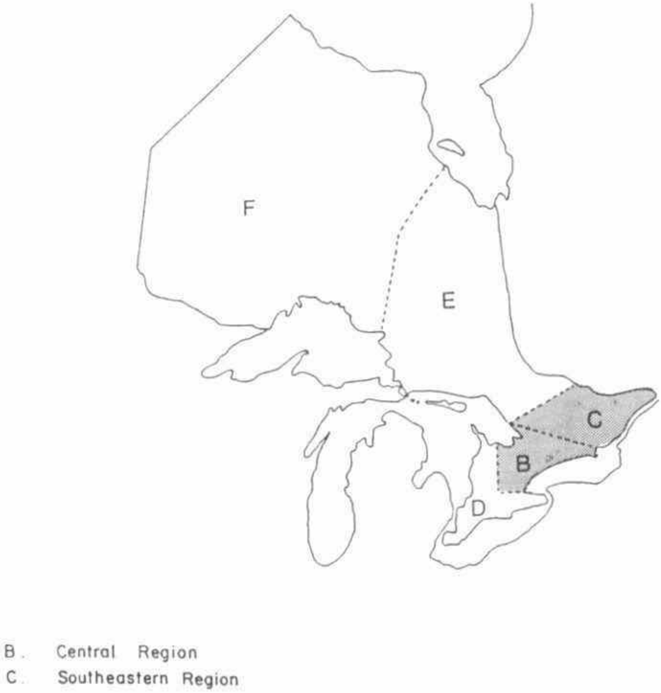
DEVELOPMENT OF ESTIMATION TECHNIQUES

Four techniques (i.e. Regression, Area Proration, Index and Isolines) for estimating low flows were developed during this study as described briefly below:

TABLE 1

SUMMARY OF LITERATURE REVIEW

Study	No. of Stations	Distribution	Method	Parameters Examined	General Form of Equations
Boyer, 1977	12	G	Regression	DA,CO,EL,LAT,LEN WF, T_{10}, R_{10}	$\ln(7Q_{10}) = f(CO,LEN,WF,T_{10},R_{10})$
Osborn, 1974	20		Index Regression	Q7L1P,P,DA,H, CL,DD	$\log 7Q_2 = f(DA,H,Q7LIP,P)$ $\log 7Q_{20} = f(P,7Q_2)$
Condie, 1983	74	G	Regression	DA,MAP,BFI	$MED(10) = f(DA, BFI)$ $GRADMEN = f((MED(10))^{.5})$
Armbruster, 1976a	104		Regression	DA,CS,BL,EL,FC MAP,ACLS,MAS,SI	$\log 7Q_{10} = f(DA, MAP, SI)$
Armbruster, 1976b				MAP,CF,DA	$\log 7Q_{20} = f(DA, MAP, CF)$
Tasker, 1975		LN III	Regression		$7Q_{10} = f(DA, MAP, T)$
Env. Can. 1978	11	G		DA,R,AS,AL,ALS, OB,LEN,DD,SLP, EL,MAP	Correlation Matrix only produced
MacLaren Plansearch, 1981	9	Eye Fit	Regression	DA,SI,ALS	$\bar{Q}_1 = f(DA, SI, ALS)$ $\bar{Q}_5 = f(DA, SI, ALS)$
Inst. of Hydrology 1980		G	Regression	$Q_{95}(10)$,BFI,DA, MAP,LEN	$Q_{95}(10) = f((BFI)^{.5}, (DA)^{.5}, (MAP)^{.5})$ $(\bar{Q}_{95}(10)) = f((BFI)^{.5}, (DA)^{.5}, (LEN)^{.5})$ $(10\bar{Q}_2) = f(BFI)$ $(10\bar{Q}_2) = f(BFI, MAP)$
Wright 1970			Regression	DA,BS,MAP	$MAM = f(DA, BS)$ $MAM = f(DA, BS, MAP)$
Inst. of Hydrology, 1986	232	LN	Regression	BFI, MAP, ACLS	$\sqrt{Q95(10)} = f(BFI, MAP, ACLS)$ $\sqrt{MAM(10)} = f(BFI, ACLS)$
Vogel & Kroll 1990	23	LN	Regression	DA, RELIEF	$7Qy = f(DA, RELIEF)$
Cumming Cockburn 1990	65	3PLN	Regression	DA,BFI,LNTH	$nQy = f(DA, BFI, LNTH)$



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STUDY REGION LOCATION

FIGURE - 1

1. Regression: Based upon the literature review, the following hydrometeorologic and physiographic parameters were selected for development of the regression equations: Hydrometeorologic; Mean Annual Precipitation, mm (MAP), Mean Annual Snowfall, mm (MAS), Mean Annual Runoff, mm (MAR) and Mean Annual Evaporation, mm (MAE) and Physiographic; Drainage Area, km^2 (DA), Area Controlled by Lakes and Swamps, % (ACLS), Stream Length, km (LNTH), 10/85 Channel Slope, m/m (SLP), Base Flow Index, dimensionless (BFI), Regulation Index, 1-regulated, 0-natural (RN), and Maximum Groundwater Fluctuation, m (GW).

   For development of the regression equations, $\log_{10}$, square root, squared and cubed transformations of these parameters and the following derived forms were used; Shape Factor 1 (SF1) = DA/LNTH^2, Shape Factor 2 (SF2) = DA/LNTH, Shape Factor 3 (SF3) = DA*SLP*LNTH/2, Infiltration/Recharge or Deep Percolation (INF) = MAP-MAR-MAS, $P1 = \left\{ LNTH/\sqrt{SLP} \right\}^{½}$ and $P2 = \left\{ BFI/(LNTH/\sqrt{SLP}) \right\}^{½}$.

   The parameters MAE and GW and the derived parameters SF1, SF2, SF3 and INF were included for the first time in this study.

   Over 250 preliminary regression equations were developed in order to predict the $7Q_2$ and $7Q_{20}$ low flows as a function of hydrometeorologic and basin physiographic parameters, parameter transforms or derived transforms. The equations were developed based on different groups of parameters as summarized in Table 2. On the basis of the highest R squares and the lowest standard error of estimates and engineering judgement, the fifth set of parameters in Group II was retained along with the other groups for testing.

2. Index Method: Graphs of $7Q_2$ and $7Q_{20}$ as a function of DA were developed for the Central, Southeastern and the combined regions. The ratio of 7Qy to various nQy (n-day flows with y years recurrence interval) were determined and plotted in Figure 2 for the three regions, respectively. Also, the ratio of 7Qy to $7Q_2$ for all these regions are depicted in Figure 2. To use this method, knowing the drainage area, the $7Q_2$ flow is estimated from the relevant graph of flow versus drainage area. If another nQy flow is required, it can be estimated by using Figure 2 depending upon the region and the type of low flow to be estimated, to determine the appropriate flow ratio as a function of $7Q_2$.

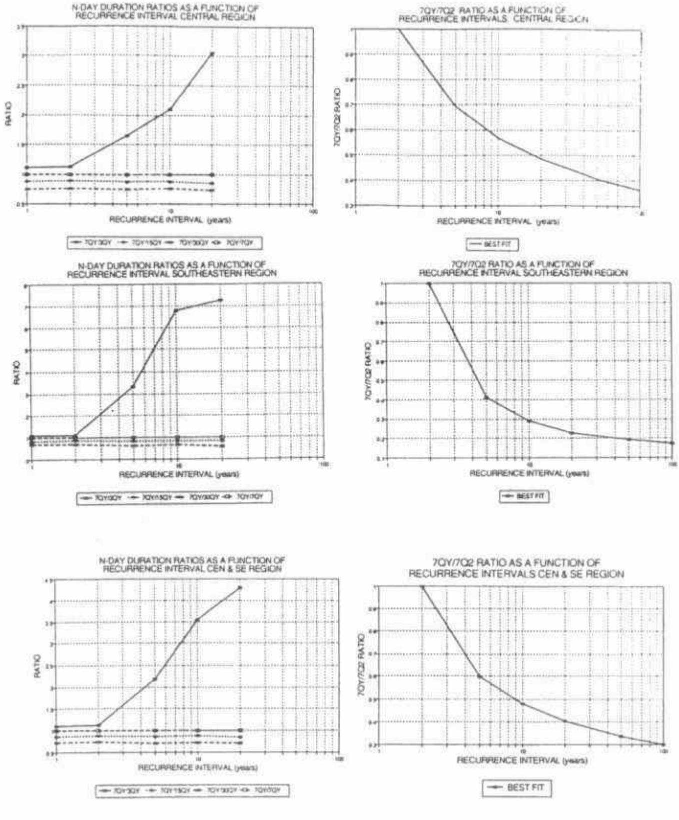
3. Area Proration: The unit area $7Q_2$ and $7Q_{20}$ low flows (L/s/km^2) were summarized for the stations in the region and the method of reciprocal distance was used as a weight in the proration estimate (i.e. the distance to nearby gauges would be estimated and unit values could then be weighted by the reciprocal of the distance and then averaged for the test stations).

4. Mapped Isolines Method: Isolines of unit area $7Q_2$ low flows were drawn using ditigal terrain modelling procedures and the $7Q_{20}$ low flows were estimated by using Figure 2.

Table 2: Summary of Regression Analysis

Group	Region	Parameter/Transformed or Derived Form	Low Flow	N	SEE	R^2
Group I	CN	MAP, DA, LNTH, RN, GW, BFI, MAS, MAE, SLP, ACLS and MAR	7Q2	48	0.52	0.86
			7Q20	48	0.25	0.72
	SE		7Q2	25	0.53	0.98
			7Q20	25	0.53	0.98
	CNSE		7Q2	73	0.98	0.91
			7Q20	73	0.61	0.89
Group II						
First Set	CN	GW^3, RN, MAP, Log10 MAE, SLP^3, SF2 AND Log10 BFI	7Q2	48	0.50	0.87
		Log10 GW, RN, INF, MAS, SLP^2, SF2, BFI^3 and ACLS	7Q20	48	0.23	0.76
	SE	Log10 GW, RN, INF, SF3, BFI^3 and MAS	7Q2	25	1.25	0.91
		Log10 GW, RN, INF, SF3, BFI^3 and ACLS	7Q20	25	0.81	0.90
	CNSE	GW^3, RN, MAP^3, MAR^3, MAE, MAS^3, SF3, BFI^3 and ACLS	7Q2	73	1.27	0.84
		GW^3, RN, MAP^3, Log10 MAR, MAE^3, MAS^3, SF3 AND BFI^3	7Q20	73	0.66	0.87
Second Set	CN	GW^3, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, EVA^3, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.50	0.87
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.45	0.99
			7Q20	25	0.27	0.99
	CNSE		7Q2	73	0.81	0.93
			7Q20	73	0.50	0.93
Third Set	CN	Log10 GW, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, MAE^3, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.50	0.87
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.47	0.99
			7Q20	25	0.29	0.99
	CNSE		7Q2	73	0.73	0.95
			7Q20	73	0.43	0.94
Fourth Set	CN	GW^3, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, Log10 MAE, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.47	0.89
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.47	0.99
			7Q20	25	0.29	0.99
	CNSE		7Q2	73	0.78	0.94
			7Q20	73	0.48	0.93
Fifth Set	CN	Log10 GW, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, Log10 MAE, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.47	0.89
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.49	0.99
			7Q20	25	0.30	0.98
	CNSE		7Q2	73	0.71	0.95
			7Q20	73	0.43	0.95
Sixth Set	CN	Log10 MAS, Log10 MAR, DA^3, BFI^2 and LNTH^2	7Q2	48	0.89	0.60
			7Q20	48	0.32	0.54
	SE		7Q2	25	0.90	0.95
			7Q20	25	0.59	0.94
	CNSE		7Q2	73	1.14	0.87
			7Q20	73	0.63	0.88
Group III	CN	MAE and DA	7Q2	48	0.64	0.79
			7Q20	48	0.29	0.61
	SE	DA, MAE and BFI	7Q2	25	0.96	0.95
			7Q20	25	0.59	0.94
	CNSE	(a) DA, GW and MAE	7Q2	73	1.27	0.84
			7Q20	73	0.80	0.81
		(b) DA, BFI and MAE	7Q2	73	1.35	0.82
			7Q20	73	0.88	0.77
Group IV	CN	DA and Log10 MAE	7Q2	48	0.62	0.80
			7Q20	48	0.29	0.62
	SE	DA^3, MAE^3 and BFI^2	7Q2	25	0.81	0.96
			7Q20	25	0.52	0.96
	CNSE	(a) DA^3, Log10 MAE and Log10 GW	7Q2	73	0.92	0.92
			7Q20	73	0.51	0.92
		(b) DA^3, Log10 MAE and BFI^3	7Q2	73	0.92	0.92
			7Q20	73	0.57	0.90
Group V	CN	DA^3, BFI^2 and LNTH^2	7Q2	48	1.02	0.48
			7Q20	48	0.35	0.45
	SE		7Q2	25	1.37	0.89
			7Q20	25	0.91	0.87
	CNSE		7Q2	73	1.23	0.85
			7Q20	73	0.65	0.87
Group VI	CN	DA only	7Q2	48	1.11	0.38
			7Q20	48	0.35	0.46
	SE		7Q2	25	2.18	0.73
			7Q20	25	1.37	0.70
	CNSE		7Q2	73	1.72	0.71
			7Q20	73	0.98	0.71

N-Number of Stations SEE-Standard Error of Estimates



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RATIOS OF DIFFERENT LOW FLOWS

FIGURE - 2

TESTING OF ESTIMATION TECHNIQUES

The relative prediction accuracy of the four methods was examined using the reserved test data set and the Nash-Sutcliffe (1970) model efficiency statistic, designated as N.S.R.^{2}. As noted previously the 21 test stations were not included in the development of the regional low flow estimation techniques.) A comparison of the test statistics is given in Table 3.

1. Regression: The estimation of low flows by the regression equations using all the untransformed parameters described by Group I was poor and, therefore, not included in further discussion. The test results for the other groups are summarized in Table 3. Based on an analysis of Table 3(b), (when stations 02KC014 and 02LB013 were excluded), it was found that the form of equation based on Group IV (DA and Log_{10} MAE for the Central region and DA^3, $\log_{10}$ MAE and BFI^3 for the combined region) and Group V (DA^3, BFI^2 and $LNTH^2$) for the Southeastern region would give acceptable accuracy. It was found that the regression method can lead to satisfactory estimation of low flows in the Central region, and acceptable accuracy in the Combined Region and a satisfactory prediction of $7Q_{20}$ in the Southeastern region. The regression equations having a very high R square value for development did not necessarily give a satisfactory N.S.R.^{2} when tested using the reserved stations.

2. Area Proration: It is evident from Table 3 that the prediction of $7Q_2$ for the Central region is good, but unsatisfactory for the Southeastern region. When both the Central and Southeastern regions are combined, the prediction is considered to be only fair. The prediction accuracy of $7Q_{20}$ is unsatisfactory for all the regions.

3. Index Method: The test results (N.S.R.^{2}) for the Central, Southeastern and Combined Regions indicate that the index method may be an appropriate prediction method for 7Q2 and $7Q_{20}$ for the Central region but does not seem to be a satisfactory prediction tool for $7Q_2$ flows in the Southeastern region. Although the number of test stations in the Southeastern region is fewer than the Central region, combining the two regions together did not improve the prediction accuracy for the Combined Region over the Southeastern region.

4. Mapped Isolines Method: The $7Q_2$ unit low flows from these maps were estimated for the Central and Southeastern regions by interpolating the values between the contour lines. The $7Q_{20}$ low flows were estimated by multiplying the estimated $7Q_2$ using the $7Q_{20}/7Q_2$ ratio determined from Figure 2. It is evident from Table 3 that the method of mapped isolines of unit low flows for the Central, Southeastern and the Combined regions appears to be a robust technique which generally tended to give the most acceptable prediction results.

DISCUSSION OF THE RESULTS

A comparison of the observed and the estimated $7Q_{20}$ low flows for the Combined region for all the methods is presented in Figure 3.

Table 3(a): The Nash-Sutcliffe, R^2!, for Testing the Estimation Techniques *

Method/ Low Flows	Central Region	Southeastern Region	Combined Region
Regression Method			
Group II (Fifth Set)			
7q20	0.24	-11.65	-1.22
7q2	0.64	-5.91	-0.04
Group III			
7q20	0.72	-15.49	(a) -2.13 (b) -7.14
7q2	0.71	-6.32	(a) -0.21 (b) -0.95
Group IV			
7q20	0.73	-6.09	(a) -0.76 (b) -0.56
7q2	0.71	-3.32	(a) -0.25 (b) -0.01
Group V			
7q20	0.40	-0.51	0.08
7q2	0.28	-0.66	0.11
Group VI			
7q20	0.67	-11.32	-2.49
7q2	0.68	-7.35	-0.50
Index Method			
7q20	0.82	-0.29	-0.67
7q2	0.83	-5.46	-0.38
Area Proration Method			
7q20	0.02	-0.63	-0.01
7q2	0.96	-0.14	0.83
Mapped Isolines Method			
7q20	0.53	0.72	0.71
7q2	0.95	0.66	0.92

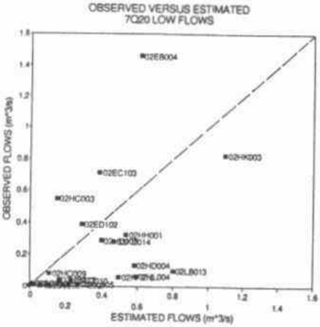
* includes stations 02KC014 and 02LB013

! N.S.R^2=1 represents perfect prediction

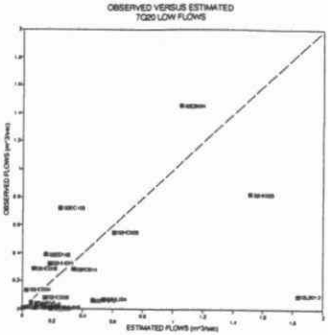
Table 3(b): The Nash-Sutcliffe, R^2, for Testing the Estimation Techniques **

Method/ Low Flows	Central Region	Southeastern Region	Combined Region
Regression Method			
Group II (Fifth Set)			
7q20	0.24	-0.57	0.03
7q2	0.64	0.01	0.47
Group III			
7q20	0.72	-0.57	(a) 0.00 (b)-2.97
7q2	0.71	0.62	(a) 0.70 (b) 0.29
Group IV			
7q20	0.73	-0.32	(a) 0.34 (b) 0.34
7q2	0.71	0.18	(a) 0.49 (b) 0.50
Group V			
7q20	0.40	0.70	0.27
7q2	0.28	-0.42	0.13
Group VI			
7q20	0.67	-1.10	-0.10
7q2	0.68	-0.39	0.44
Index Method			
7q20	0.82	0.92	0.44
7q2	0.83	-0.12	0.45
Area Proration Method			
7q20	0.02	-0.18	0.04
7q2	0.96	0.12	0.86
Mapped Isolines Method			
7q20	0.53	0.73	0.75
7q2	0.95	0.89	0.95

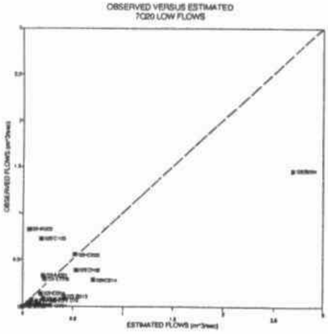
** excludes stations 02KC014 and 02LB01 3 due to effects of regulation



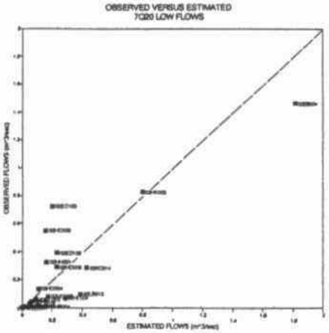
REGRESSION (NSR^2 0.34)



INDEX (NSR^2 0.44)



AREA PRORATION (NSR^2 0.04)



MAPPED ISOLINES (NSR^2 0.75)

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TEST STATIONS OBSERVED Vs ESTIMATED
7 Q 20 COMBINED REGIONS

FIGURE . 3

The prediction techniques which were developed equal or exceed the accuracy of the methods identified in the literature review.

In general it was found that for estimation of low flows in the Central region, any one of the methods (i.e. index, regression or mapped isoline) can be used satisfactorily. However, for the Southeastern (and hence for the Combined regions), the method of mapped isolines was found to be the most consistent for satisfactory estimation of low flows. Refinement of the regression technique for watersheds in the Southeastern region appears to require additional investigation including definition and incorporation of other watershed parameters in order to sufficiently explain low flow characteristics.

RECOMMENDATIONS FOR FUTURE STUDY

It is recommended that similar low flow prediction techniques be developed for other regions of Ontario. Further investigation should also be undertaken for watersheds located in the Southeastern region to develop appropriate watershed parameters for refining low flow estimates.

ACKNOWLEDGEMENT

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B8

RETRACTABLE COMPOSITE ABSORBENTS FOR ENVIRONMENTAL CLEAN-UP.

B.Gillies* and H.Auksi, Eco Corp., Willowdale, Ontario, M2H 3B4
O.Meresz, Ministry of the Environment, Rexdale, Ontario, M9W 5L1

INTRODUCTION

Chemical spills into lakes and rivers constitute a source of contamination to the water supply. Some of these chemicals sink to the sediments and eventually dissolve into the water. The immobilization and clean-up of chemical spills is required to minimise dissolution of the contaminant to the water. In the previous project (#375C), a crosslinked polymer absorbent was developed that is capable of removing a range of chemicals from water. In Project #456C, the retractable absorbent was tested under field conditions. The results of this field trial will be presented.

CROSSLINKED POLYMER ABSORBENT

Upon exposure to a chlorinated solvent, crosslinked ethylene vinyl acetate (EVA) will absorb the solvent and swell. Absorption continues until the polymer cannot expand any further due to the crosslinked nature of the absorbent.

Pilot scale production of crosslinked EVA beads was carried out using an EcoPlastics custom built reactor, a stainless steel vessel containing a rotating ribbon. EVA beads and hexane, containing the desired amount of dissolved initiator lauroyl peroxide, were added to the reactor and the beads were soaked for one hour in a controlled nitrogen atmosphere. The reactor was flushed again with nitrogen for an hour, and then heated to 60°C. The beads were heated at this temperature until the initiator had undergone several half-lives, approximately 27 hours.

Lab scale evaluation of the crosslinked EVA beads showed that they had absorption capacities in the range of 20 g tetrachloroethylene/g polymer, had good structural integrity after absorption of the chemical, showed a low rate of release of absorbed chemicals into the water stream, and were easily placed and retrieved from a simulated river bed without detectable loss of the absorbed solvent.

FIELD TRIAL

SITE

In order to demonstrate the effectiveness of the technology, a field trial was conducted. The site chosen was that of the 1985 spill of tetrachloroethylene in the St. Clair River. The initial spill of 11,000 L was recovered, but small pools are still seen. A grid system was set up over the 50 m x 50 m clean-up area to monitor the appearance of any pools of tetrachloroethylene. There is very little material currently present. During an annual quarterly inspection in the Spring of 1990, around 2 L of a dark brown liquid were collected. This liquid mixture contained tetrachloroethylene and carbon tetrachloride in an approximate ratio of 7:3.

The river bottom is generally flat and sandy. In the Fall of 1989, the area was disturbed to install a collection system for any solvent pools that might accumulate. Trenches were dug and most of the area was backfilled with coarse gravel.

ABSORBENT MATS

The absorbent beads were sewn into mats (500 g absorbent/mat). The mats were designed to withstand the rigorous conditions that could be expected on the river bottom. The 2 ft x 2 ft mats were made of a vinyl coated fibreglass screen, with holes of around 1.5 mm x 2.5 mm which would allow any chemical spill material to pass through into contact with the absorbent material within the mats.

A diver recorded the location of pools of solvent on the river bottom. The size of most of these pools ranged from "dime" size to "quarter" size. The smallest pools were tiny beads, and the largest pool was around 4 inches x 2 inches. The diver returned to some of those areas with the mats and staked them into the sediment. A total of eight mats were staked down. Two of the mats were placed in control areas where no solvent pools were observed, one at the upstream boundary of the grid study site, and one in the middle of the study site.

After 20 days, the mats were retrieved from the river bottom. Upon retrieval, the diver noted that the mats had been covered with a dusting of sediment, which was a half an inch thick in some places.

After the stakes were removed, each mat was placed in its own 6 mil thick polyethylene bag, most of the water was squeezed out, then the bag was sealed. Each mat was therefore protected from cross-contamination. The bags containing the mats were brought to the surface and placed in drums for transportation to Eco Corp. Research Centre for analysis.

ANALYSIS OF THE ABSORBENT RETRIEVED FROM THE ST. CLAIR RIVER BOTTOM

GENERAL COMMENTS

The mats that were placed in the areas where pools were observed had a distinct odour of chlorinated solvents. Some of the beads within these mats were coloured dark brown indicating absorption of the chemical pools. These dark beads were in patches, indicating that the pools that had made contact with the beads were absorbed. Other beads in these mats ranged in colour from light brown to light gold. The mats that were not placed directly over observed pools had an odour of algal growth. These beads also had a slight yellow colour.

MASS OF MATERIAL RETRIEVED

The mass of liquid absorbed by the polymer beads was measured as follows. The beads were removed from each mat, washed in tap water to remove any sand, patted dry on paper towels, then weighed. The weight of crosslinked beads (500 g) which had been similarly soaked in water, washed and dried was subtracted from the weight of beads from each mat obtained above. The resulting masses of material within the beads is shown in Table 1. The total mass of solvent material retrieved is around 218 g.

Table 1. Mass of material in the absorbent beads retrieved from the St. Clair River bottom, after washing the beads and patting them dry.

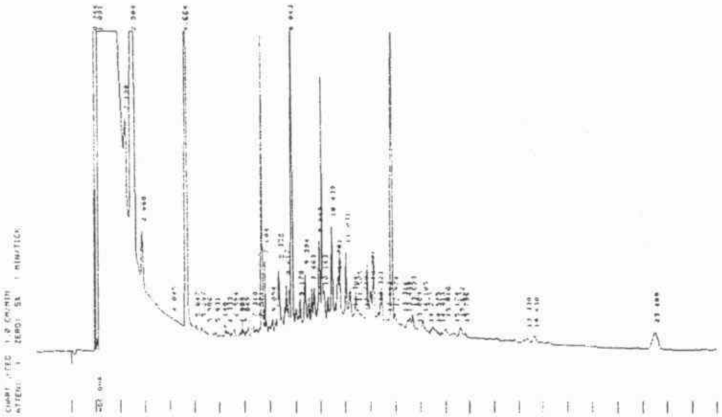
Sample Mat		Mass of Absorbed Material In Beads (g)
ECO-101	Pools observed	14
ECO-102	Pools observed	46
ECO-103	Pools observed	21
ECO-104	Pools observed	63
ECO-105	Pools observed	28
ECO-106	Pools observed	25
ECO-107	No pools observed	13
ECO-108	No pools observed	8

IDENTIFICATION OF MATERIAL ABSORBED

Samples of the beads were extracted in methylene chloride and analyzed by gas chromatography using a flame ionization detector. Figure 1 shows the existence of many other significant peaks besides that from tetrachloroethylene. Under these conditions, tetrachloroethylene has a residence time of 4.66 min. The methylene chloride gives rise to the large peak at 1.09 min., and an impurity in the methylene chloride gives a peak at 2.5 min.

At the time of writing, analysis of the retrieved material has not been completed. However, it appears that the polymer will absorb many other trace compounds.

Figure 1. Chromatogram of a methylene chloride extract of the beads retrieved from the river bottom.
Column type: DB-1, 0.32 mm ID, 30 m long
Temperature program: 70°C for 3 min.,
20 °C/min. to 220°C,
isothermal for 15 min.
Carrier gas: He, 6.5 mL/min.



ABSORPTION OF TRACE AMOUNTS OF CHEMICALS FROM WATER

Tetrachloroethylene was observed in the methylene chloride extracts of the beads from all of the mats. Methylene chloride extracts from the beads of mats placed in areas where no pools of chemicals were observed showed the presence of trace amounts of tetrachloroethylene. This indicates that the beads will also act as an absorbent of trace amounts of chemicals dissolved in water or in the sediment.

The ability of crosslinked EVA to pick up tetrachloroethylene from solution without direct contact with the bulk phase was confirmed in laboratory studies. Beads placed in water containing dissolved tetrachloroethylene were removed and dried, then extracted in methylene chloride. The methylene chloride extracts were analyzed by gas chromatography and showed the presence of tetrachloroethylene.

SUMMARY

The crosslinked absorbent placed in screen mats performed as expected. In areas where pools of solvent were observed, the bulk solvent was absorbed if direct contact was made with the mat. Some trace amounts of tetrachloroethylene were absorbed from the water or sediment by all of the mats. Although there was very little pooled material visibly present on the river bottom (less than 2 L had accumulated over a four month period), the polymer absorbent in the mats collected around 200 g of this material over the twenty day period of the trial. The mats, which covered around 0.12 % of the 50 m x 50 m study site picked up around 6 % of the 2 L of material recovered by vacuuming.

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B9

ADVANCED TECHNOLOGY FOR DESTRUCTION OF ORGANIC POLLUTANTS IN WATER STREAMS

Hussain Al-Ekabi, Ali Safarzadeh-Amiri, Joan Story, Wendy Holden & Gail Edwards*

Nulite, a division of Nutech Energy Systems Inc.
317 Consortium Court
London, Ontario N6E 2S8

INTRODUCTION

The environment is contaminated on a global level with a variety of toxic pollutants that come to the environment from various sources. The level of these pollutants (mostly organic) has now increased to the point that immediate and innovative action is needed to address the problem.

Conventional pollution treatment technologies, such as carbon adsorption, air stripping and bio-oxidation, are effective in removing many organic pollutants from water streams, but they exhibit a major drawback. Both carbon adsorption and air stripping merely transfer the organic pollutants from one medium to the other. Biological treatment, on the other hand, is relatively slow and inefficient in removing many man-made organic pollutants such as chlorinated hydrocarbons. An efficient technology is required, which will not only remove the organic pollutants from the water streams, but also destroy them.

Among advanced photo-oxidation processes, the TiO_2 photocatalyzed removal of organic pollutants has recently begun to show considerable promise (1 - 4). The TiO_2 photocatalytic degradation of various organic compounds by illuminated TiO_2 is very well documented in literature (see for instance references 5 - 13). The illumination of TiO_2 in water with light of wavelength <400 nm generates excess electrons in the conduction band (e^-_{CB}) and positive holes (h^+_{VB}) in the valence band (Figure 1).

$$TiO_2 + h\nu \text{ -------> } e^-_{CB} + h^+_{VB} \qquad (1)$$

At the surface the holes either react with adsorbed H_2O or surface OH^- groups to form $\cdot OH$ radicals.

$$h^{+}_{VB} + H_2O(ads.) \text{ -------> } \cdot OH + H^{+} \qquad (2a)$$

$$h^{+}_{VB} + OH^{-}(sur.) \text{ -------> } \cdot OH \qquad (2b)$$

Excess electrons in the conduction band probably react with molecular oxygen to form superoxide ions

$$e^{-}_{CB} + O_2 \text{ -------> } O_2^{\cdot -} \qquad (3)$$

which can further disproportionate to form more $\cdot OH$ radicals.

$$2O_2^{\cdot -} + 2H_2O \text{ -------> } 2 \cdot OH + 2OH^{-} + O_2 \qquad (4)$$

The $\cdot OH$ radicals are extremely reactive and readily attack organic molecules, eventually degrading them to CO_2 and H_2O (and halide ions when the organic molecule contains halogen atoms). Thus the advantage of this technology is that it not only removes, but also destroys organic pollutants.

EXPERIMENTAL SECTION

The patented Nulite photoreactor (14) comprises a jacket, a lamp and a photocatalytic sleeve. The lamp emits ultraviolet light in the 300 - 400 nm range and is mounted coaxially within the jacket. Around the lamp lies a sleeve formed of fibreglass mesh that is coated with titanium dioxide (anatase). The anatase is activated by ultraviolet light. Contaminated water flows through the reactor in parallel with the lamp. Typically, 4 L of contaminated water was circulated through the system for 15 min in the dark. At this point the light was switched on and analyzed on a Hewlett Packard 5890A gas chromatograph using a megabore DB-5 (30 m long, 0.53 mm in diameter) with an electron capture detector operating at 300 °C and nitrogen (14 mL/min) was used as carrier gas.

RESULTS AND DISCUSSION

The major practical problem in using TiO_2 as a photocatalyst is the "hole-electron" recombination process. This process is efficient and considered as the principal energy wasting step in the TiO_2 photocatalytic degradation of organic pollutants. The low quantum yield (< 5%) of the TiO_2 photocatalytic degradation of organic compounds is indicative of the effect of the "hole-electron" recombination process.

A challenging opportunity does exist to improve the degradation rate of organic pollutants by preventing the "hole-electron" recombination process. This is an important step prior to commercial application of the TiO_2 technology for water treatment.

One attractive strategy for inhibiting the "hole-electron" recombination process is to add efficient (preferably irreversible) electron acceptors to the reaction. In order for these additives to efficiently inhibit the recombination process they should fulfil the following criteria: (a) readily accept the superoxide ions ($O_2^{\cdot -}$), (b) rapidly dissociate into harmless products and (c) provide additional routes for the formation of $^{\cdot}OH$ radicals or other powerful oxidizing agents. We have examined four additives: oxygen, hydrogen peroxide, ozone and ammonium persulphate and have found the results very promising.

i. Effect of Oxygen

The presence of oxygen proves essential for the TiO_2 photocatalytic degradation of organic compounds to be efficient. Figure 2 shows, for comparison, the degradation of 2,4-dichlorophenol under nitrogen, oxygen and our usual air atmosphere (no gas added) conditions. It is evident that when nitrogen was introduced the degradation rate decreased remarkably. However, introducing oxygen led to an 80% increase in the degradation rate of 2,4-DCP. Similar results were obtained when air was introduced in the line just before the reactor. Evidently, oxygen traps the conduction band electron to form superoxide ions ($O_2^{\cdot-}$) and thus prolongs the lifetime of the photogenerated "hole" which is necessary for $^{\cdot}OH$ radical production. The superoxide ions could disproportionate as in equation (4) to form further $^{\cdot}OH$ hydroxyl radicals.

ii. Effect of Hydrogen Peroxide

The simplest process available for the generation of hydroxyl radicals is the direct photochemical cleavage of hydrogen peroxide. However, this process is usually associated with serious practical problems. The exceptionally low molar extinction coefficient of hydrogen peroxide, and the necessity of using expensive UV light (200-300 nm) are obvious problems. The efficiency of the process is very susceptible to high levels of suspended solids and other light absorbing substances present in water.

Our approach is not to irradiate H_2O_2 directly, but instead to use H_2O_2 as an irreversible electron acceptor. On accepting an electron, either from the conduction band or the superoxide ion, hydrogen peroxide decomposes according to the following equations (15):

$$H_2O_2 + e^-_{CB} \text{ -------> } {}^{\cdot}OH + OH^- \tag{5a}$$

$$H_2O_2 + O_2^{\cdot-} \text{ -------> } {}^{\cdot}OH + OH^- + O_2 \tag{5b}$$

Obviously, this will not only prolong the lifetime of the valence band "hole" as previously discussed, but it will also provide an additional route for $^{\cdot}OH$ radical formation. We have examined the effect of H_2O_2 on the degradation of a mixture of organic pollutants containing *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and

2,4,6-trichlorophenol (10 ppm each). Figure 3 illustrates the degradation of these components as a function of irradiation time in the absence and presence of H_2O_2. Clearly our results show that H_2O_2 markedly increases the degradation rates of all the components involved in this mixture.

iii. Effect of Ozone

Ozone is currently used in some industrial advanced photo-oxidation processes. In these processes ozone is directly irradiated by UV light, as is the case with H_2O_2, therefore we have chosen to use ozone as an irreversible electron acceptor.

The formation of ozonide ion ($O_3^{\cdot-}$) through electron transfer from the conduction band of the TiO_2 to ozone, has been established for some time (16) although no attempt has been made to use ozone as an irreversible electron acceptor in the TiO_2 photocatalytic degradation of organic compounds in aqueous solutions. In fact, $O_3^{\cdot-}$ can also be formed by electron transfer from the superoxide ion to ozone.

$$O_3 + e^-_{CB} \text{ -------> } O_3^{\cdot-} \tag{6a}$$

$$O_3 + O_2^{\cdot-} \text{ -------> } O_3^{\cdot-} + O_2 \tag{6b}$$

The ozonide ion in water reacts with a proton to form $^{\cdot}OH$ radicals.

$$O_3^{\cdot-} + H^+ \text{ -------> } {}^{\cdot}OH + O_2 \tag{7}$$

Thus, the addition of ozone to the TiO_2 photocatalytic process is expected to provide more $^{\cdot}OH$ radicals.

Recently we independently examined the TiO_2 photocatalytic degradation of 2,4-dichlorophenol and nitrobenzene in the presence and absence of ozone, and have found that ozone markedly increased the photodegradation rates of these compounds. Control experiments showed that ozone in the dark (no light in the reactor) also degrades these compounds, although at a lower rate than those experiments where light is present in the photoreactor. We should mention that under our conditions, ozone does not absorb the light since our lamps have very little output below 300 nm.

iv. Effect of Ammonium Persulphate

In many industrial wastes, where degradation of organic pollutants is the major concern, the addition of an inorganic anion (such as persulphate ion) to enhance the degradation rate of the organic pollutants may be justified. In homogeneous reactions the persulphate ion dissociates, on accepting an electron, to a sulphate ion and a sulphate radical ion (17).

$$S_2O_8^{2-} + e^- \text{-------}> SO_4^{-\cdot} + SO_4^{2-} \qquad (8)$$

Based on this experimental fact, we have chosen ammonium persulphate as an electron acceptor in the photocatalytic degradation of organic pollutants with the hope that, under our conditions, $S_2O_8^{-\cdot}$ could also accept an electron from the conduction band or the superoxide ion ($O_2^{\cdot -}$) to give SO_4^{2-} and $SO_4^{-\cdot}$

The sulphate radical ion is effective in two ways: (a) it can act as a precursor for $^{\cdot}OH$ radicals as shown in the following equation:

$$SO_4^{-\cdot} + H_2O \text{-------}> SO_4^{2-} + {}^{\cdot}OH + H^+ \qquad (9)$$

and (b) it could act as a powerful oxidizing agent for organic pollutants.

We have examined the degradation of a mixture of *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol (10 ppm each) in the presence and absence of persulphate ions. The results presented in Figure 4 show clearly that $S_2O_8^{2-}$ markedly increased the degradation rates of the four components involved in the reaction mixture.

CONCLUSIONS

Our results clearly indicate that the TiO_2 photocatalytic degradation of organic pollutants by the Nulite reactor opens a good opportunity for water treatment. The TiO_2 process will offer a clean, inexpensive and simple technology to remove organic pollutants from water streams.

ACKNOWLEDGEMENTS

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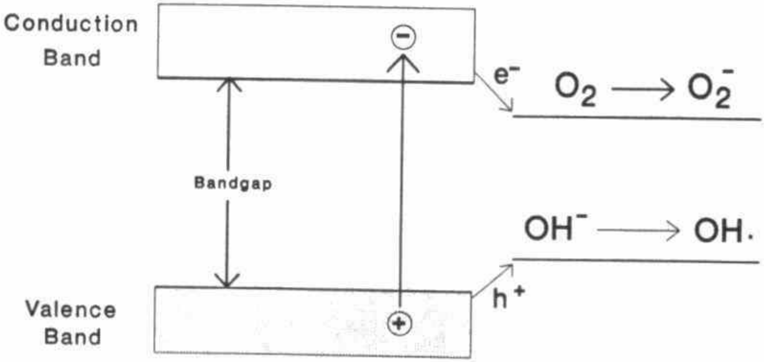

Figure 1: Reduction of oxygen by the conduction band electron and oxidation of hydroxyl group by the valence band hole.

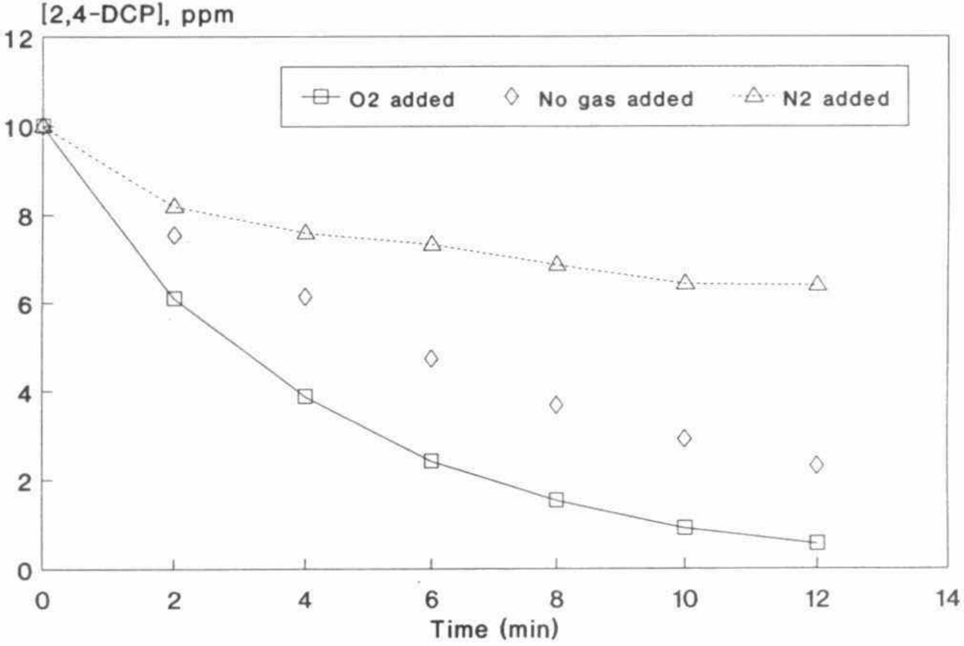

Figure 2: The photocatalytic degradation of 2,4-dichlorophenol in open system (no gas added), under nitrogen and under oxygen.

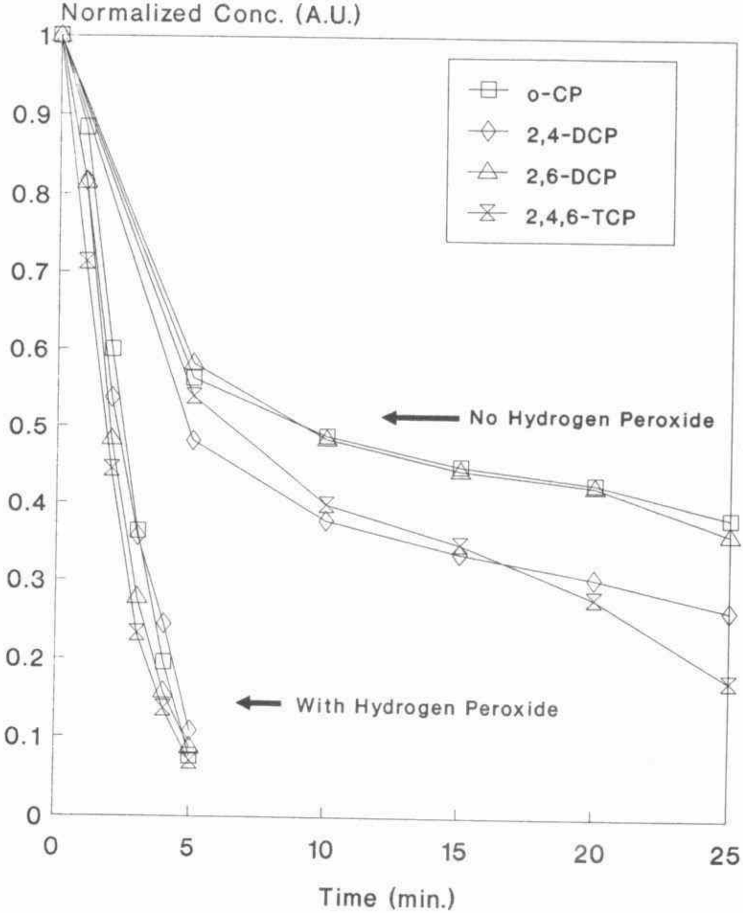

Figure 3: The photocatalytic degradation of a mixture of four chlorinated phenols (10 ppm each) in the presence and absence of hydrogen peroxide.

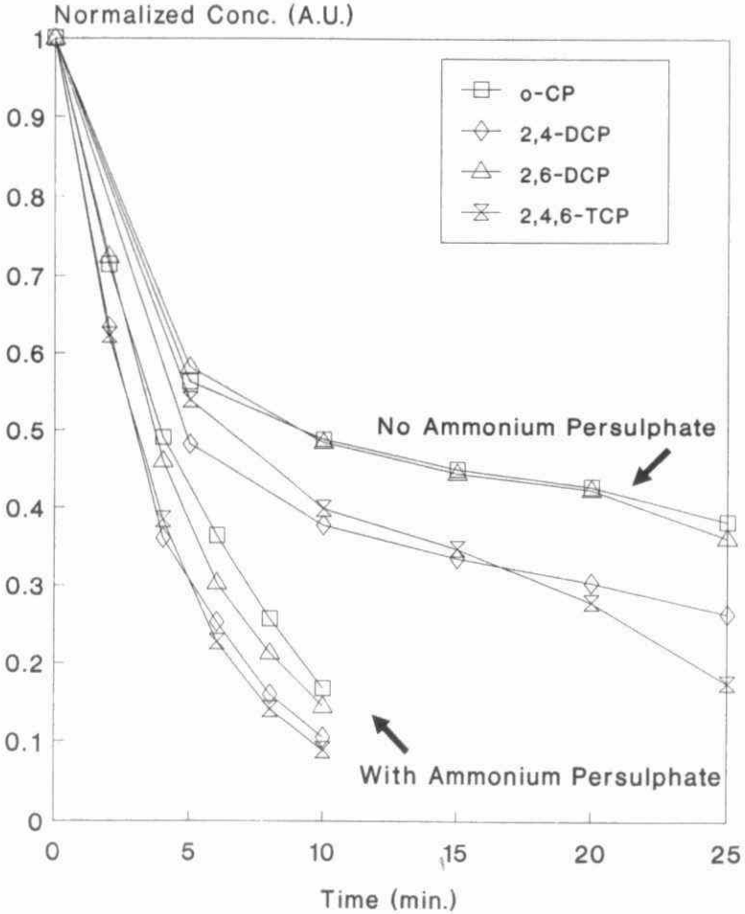

Figure 4: The photocatalytic degradation of a mixture of four chlorinated phenols (10 ppm each) in the presence and absence of ammonium persulphate.

B11

CARCINOGENICITY TESTING OF BLEACHED KRAFT MILL EFFLUENT USING IN VIVO RAINBOW TROUT ASSAYS

C.D. Metcalfe, M.E. Nanni and N.M. Scully
Environmental and Resource Studies, Trent University, Peterborough, Ontario K9J 7B8

ABSTRACT

In vivo assays with rainbow trout are being used to determine whether bleached kraft mill effluent (BKME) is carcinogenic to fish. BKME extracts were prepared by column chromatography with XAD resins. Non-polar to medium polarity compounds were extracted using XAD-4 resin, and polar compounds were extracted using XAD-7 resin. Ames-positive mutagens are present in the XAD-7 extract, and the XAD-4 extract induces elevated aryl hydrocarbon hydroxylase activity and peroxisome proliferation activity in hepatocytes after intraperitoneal injection into rainbow trout. In vivo experiments are in progress to determine whether BKME extracts are carcinogenic to rainbow trout, or act as promotional agents in the development of aflatoxin B_1-induced tumours.

INTRODUCTION

Bleached kraft mill effluents (BKME) have been shown to have mutagenic activity (1, 2), and to induce physiological disturbances in fish, including induction of cytochrome P450 dependent-monooxygenases (3, 4). In addition, white sucker populations in close proximity to bleached kraft pulp mills have been reported to have a high prevalence of liver tumours and "liver disease" (5). In this study, in vivo bioassays with rainbow trout are being used to identify the toxic and carcinogenic effects of BKME to fish.

Extracts of BKME were prepared with XAD macroreticular resins. Non-polar to medium polarity compounds were extracted with XAD-4 resin, and polar compounds were extracted with XAD-7 resin. These extracts were injected intraperitoneally into rainbow trout in both short-term and long-term bioassays to determine carcinogenic activity, promotional activity, ability to induce cytochrome P450-dependent aryl hydrocarbon hydroxylase (AHH) activity in hepatocytes, and ability to induce proliferation of peroxisomes in hepatocytes. The latter toxic response (peroxisome proliferation) is thought to be involved in a carcinogenic process which does not involve genotoxicity and requires chronic exposure to the carcinogenic agent (6, 7).

It is anticipated that these studies will aid in determining whether BKME are carcinogenic to fish. These data will also identify the classes of compounds which are responsible for the toxic/carcinogenic/genotoxic activity of BKME.

METHODS

Preparation of Extracts:

BKME were obtained as "grab" samples from the Canadian Pacific Forest Products kraft mill in Thunder Bay, Ontario. BKME were filtered in aliquots of 2 L through a 0.3 μm glass fibre filter (GFC). The GFC was extracted into methanol in a soxhlet apparatus. The filtrate was divided into 2 aliquots. One aliquot was passed through Amberlite XAD-4 resin, and non-polar to medium polarity compounds adsorbed to this resin were eluted with 100 mL of diethyl ether. The other aliquot was passed through Amberlite XAD-7 resin, and polar compounds adsorbed to the resin were eluted with 100 mL of methanol. All extracts were concentrated by rotary evaporation and made up to a final volume in acetone. Thus, 3 extracts were produced from each effluent sample: i) Filter extract, ii) XAD-4 extract, and iii) XAD-7 extract. Extracts were diluted with appropriate carrier solvents, and doses for in vitro and in vivo assays were calculated in terms of "mL equivalents" of the original effluent volume.

Carcinogenicity Assay:

Rainbow trout (Oncorhynchus mykiss) were injected with test chemicals and extracts in the sac fry stage using the methods described by Metcalfe et al. (8), or trout eggs were immersed in solutions of test chemicals according to the aqueous immersion protocol described by Hendricks (9) In some treatments, early life stages of trout were exposed to two test treatments by both of these methods. At 2 additional points during the development of the fish (at 2 mo and 5 mo), some of the trout were injected intraperitoneally with test extracts, using the methods described by Kotsanis and Metcalfe (10). Table 1 lists the treatments and numbers of dosed animals remaining in the trout carcinogenicity assays currently underway. The promotional activity of XAD-4 extract is being assayed after initiation with the potent fish hepatocarcinogen, aflatoxin B_1.

Mutagenicity Assay:

Effluent extracts were tested for mutagenic activity with the Ames fluctuation assay (11), using Salmonella typhimurium tester strains TA100 and TA98, with and without exogenous activation with rat S-9. Extracts were tested at doses between 25 and 200 mL equivalents per test well.

Assay for AHH Induction:

Rainbow trout (3 fish per treatment) weighing approximately 300 g were anesthetized with quinaldine sulfate and injected intraperitoneally with 4 doses (0.8, 8, 80 and 160 mL equivalents/kg) of each of the effluent extracts, or carrier solutions (negative control), or β-napthoflavone (positive control) at a dose of 100 mg/kg. After dosing, the fish were placed in water at 12°C for 72 h.

At 72 h post-dosing, the fish were sacrificed with an overdose of MS-222. The livers were removed and placed in cold 1.15% KCl. The livers were homogenized and a microsomal solution prepared according to the method described by Guengerich (12). The microsomal praparation was stored in liquid nitrogen until AHH activity was assayed. The AHH activity was determined by the method described by Nebert and Gelboin (13). Activity was expressed as fluorescence units per mg of protein per minute of incubation. Protein content of the microsomal preparation was determined using the method described by Bradford (14).

Assay for Peroxisome Proliferation:

Rainbow trout (3 fish per treatment) weighing approximately 100 g were injected as described for the AHH assay with 3 doses (16, 80, 160 mL equivalents/Kg) of each of the effluent extracts, or carrier solutions (negative control), or di-(2-ethylhexyl)phthalate (positive control) at doses of 2, 1 and 0.2 g/kg. Fish were subsequently placed in water at 12°C for 5 days.

At 5 days post-dosing, fish were sacrificed as described above, and small pieces of liver tissue were fixed in cold 2.5% glutaraldehyde/0.1 M cacodylate buffer (pH 7.4) for 3-6 h. The tissues were then washed for 2 to 4 h in 0.1 M cacodylate buffer and incubated at 37°C for 30 to 60 min in diamino-benzidine (DAB) medium, according to the method described by Novikoff and Goldfischer (15). After DAB incubation, the tissues were post-fixed with osmium tetroxide, embedded in Epon, sectioned with an ultramicrotome, and examined by transmission electron microscopy (TEM) for evidence of proliferation of cellular peroxisomes in hepatocytes. Alternatively, thick sections (1-5 μm) of Epon-embedded tissues were prepared, stained with toluidine blue (16), and examined for evidence of peroxisomal proliferation by light microscopy (x1500 magnification).

RESULTS AND DISCUSSION

The XAD-7 and XAD-4 extracts of bleached kraft mill effluent gave different biological responses. However, filter extracts gave no response in the in vitro assay for mutagenicity, or the in vivo assays for induction of AHH activity and peroxisome proliferation.

Mutagenicity, as determined in the Ames fluctuation assay, was primarily confined to the XAD-7 extract containing relatively polar compounds (Table 2), although there was a slight response in tests with a high dose of XAD-4 extract. Therefore, as has been reported for other kraft mill effluents (1, 2), the majority of mutagenic activity in these effluents is confined to a fraction containing water-soluble compounds. Mutagenic activity was only seen in tests with the TA100 tester strain, both with and without addition of rat S-9. Thus, the mutagenic constituents of the XAD-7 extract are direct-acting mutagens that produce base-pair substitutions in bacterial DNA. However, mutagenicity was not observed when XAD-7 extract was tested at similar doses in the Ames plate incorporation assay. This observation indicates that mutagenic compounds in the effluent extract are relatively labile, as has been noted in other studies (1).

The data summarized in Figure 1 indicates that AHH activity was elevated above background levels by both XAD-4 and XAD-7 extracts, but induction data at the highest doses of effluent extracts (160 mL equivalents/kg) indicate that compounds in the XAD-4 extract are the most potent inducers of hepatic AHH activity. Thus, relatively non-polar compounds are responsible for this biological response. Although it has been reported previously that in situ exposure of fish to BKME elevates levels of hepatic cytochrome P450-dependent monooxygenases (3, 4), the active compounds in BKME have not previously been characterized according to chemical polarity. In the future, we will test the effluent extracts for ability to induce hepatic 7-ethoxyresorufin-o-deethylase (EROD) activity in rainbow trout; a monooxygenase reponse which is reportedly elevated more dramatically after BKME exposure than the AHH response (3, 4). The induction of cytochrome P450-dependent monooxygenases in fish exposed to BKME is significant because induction of these hepatic enzymes may alter the metabolism of other carcinogenic substances, or chronic induction of these MFO enzymes may have a promotional effect upon tumour development.

Induction of proliferation of cellular peroxisomes by certain classes of chemicals, including phthalate plasticizers, has been correlated with the development of hepatic tumours in rodent models (6, 7). Tumourigenesis generally requires chronic dosing with chemicals. It also appears that the mechanism of carcinogenesis with "peroxisome proliferators" does not involve genotoxicity, as is the case with "classic" carcinogens. It is possible that BKME may be carcinogenic to fish as a result of chronic exposure to peroxisome proliferator substances, rather than genotoxic chemicals.

As summarized in Table 3, the highest dose of the XAD-4 extract induced the formation of cytoplasmic organelles in hepatocytes, which resemble peroxisomes in size and staining characteristics. These organelles were visible by TEM and light microscopy, and they resembled the organelles induced by the positive control compound, DEHP. Similar responses were not observed in the XAD-7 treatments or the filter extract treatments, although there was evidence of hepatocellular necrosis in the XAD-7 treatments. In addition to the induction of peroxisome-like organelles in the XAD-4 treatment (high dose), increased amounts of smooth ER were also visible in the hepatocytes of these fish. This response, which has also been noted in rodents exposed to peroxisome proliferators (17), may be correlated with increased cytochrome P450-dependent monooxygenases in the liver. Studies are continuing on this response to BKME, including analysis of trout hepatic catalase activity, which is also correlated with peroxisome proliferation (18).

The carcinogenicity bioassay for trout exposed to BKME extracts is in the 7th mo of a scheduled 10 mo duration. At the end of the assay, fish will be sacrificed and liver tissues will be prepared for a histopathological survey of tumour incidence in the various treatments. Other tissues will be examined grossly for evidence of tumour development, and, if necessary, prepared for histological confirmation of malignancy.

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Ian Smith of the OME Rexdale Laboratory provided technical advice on the AHH and EROD assays and expedited sampling of kraft mill effluents. Dave Rokosh of the Rexdale Laboratory provided data on the Ames fluctuation assay of effluent extracts. D. Murray of the OME District Office at Thunder Bay arranged for collection of effluent samples.

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Table 1: Summary of treatments in the rainbow trout carcinogenicity assay of BKME.

TREATMENT		NUMBER REMAINING (7 Mo)
Egg/Fry Exposure	I.P. Injection	
AFB1[1]	-	120
AFB1[1] plus XAD-4[2]	-	114
AFB1[1] plus XAD-4[2]	XAD-4[3]	96
XAD-7[4]	-	118
XAD-7[4] plus XAD-4[2]	-	113
XAD-7[4] plus XAD-4[2]	XAD-4[3]	93
XAD-4[2]	-	111
XAD-4[2]	XAD-4[3]	85

1) Trout eggs exposed by aqueous immersion to a solution of aflatoxin B_1, at a concentration of 0.25 μg/mL for 1 h.

2) Trout sac fry exposed by microinjection of extract (0.5 μl volume) at a dose of 0.05 mL equivalents per sac fry.

3) Trout juveniles exposed by i.p. injection at 2 mo and 5 mo to the extract, at a dose of 500 mL equivalents/kg.

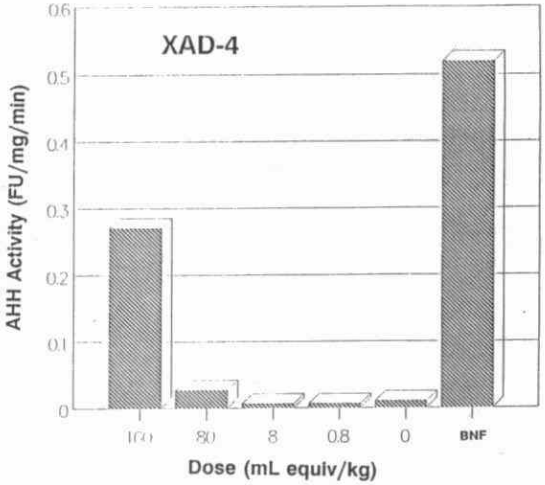
4) Trout eggs exposed by aqueous immersion to a solution of XAD-7 extract, at a concentration of 3.4 mL equivalents/mL for 6 h.

Table 2: Mutagenic response to BKME extracts in the Ames fluctuation assay. Effluent samples were tested with Salmonella strains TA98 and TA100, with and without addition of rat S-9.

EXTRACT	RESPONSE				LOWEST DOSE SHOWING RESPONSE (mL equiv.)
	TA98	TA98S[1]	TA100	TA100S[1]	
Filter	-	-	-	-	-
XAD-4	-	-	+/-[2]	+/-[2]	40
XAD-7	-	-	+	+	4.25

1) Assays run with addition of rat S-9.

2) Weak response.



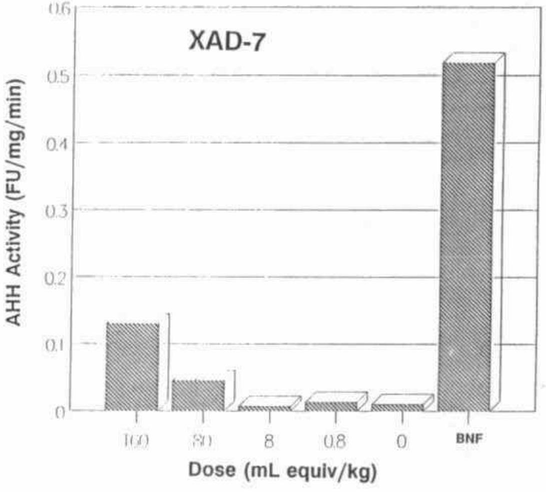


Table 2: Mean AHH activity (3 fish per dose), expressed as fluorescence units per mg protein per minute of incubation, in rainbow trout liver after exposure by i.p. injection to XAD-4 and XAD-7 extracts from BKME, or β-naphthoflavone (100 mg/kg).

Table 3: Ultrastructural (TEM) response of rainbow trout hepatocytes to exposure to BKME extracts and DEHP (positive control). Three trout were dosed per treatment.

TREATMENT	CONCENTRATION	RESPONSE
XAD-4	160 mL equiv/kg	P[1]
	80 mL equiv/kg	N[2]
	16 mL equiv/kg	N
XAD-7	160 mL equiv/kg	N
	80 mL equiv/kg	N
	16 mL equiv/kg	N
Filter	160 mL equiv/kg	-[3]
	80 mL equiv/kg	-
	16 mL equiv/kg	-
DEHP (Positive Control)	2g/kg	P
	1g/kg	P
	0.2g/kg	P
Negative Control		-

1) Proliferation of peroxisomes.

2) Evidence of necrosis among hepatocytes.

3) No response.

B12

IMPACT OF BLEACHED KRAFT MILL EFFLUENT (BKME) ON FISH POPULATIONS NEAR TERRACE BAY, ONTARIO.

M.E. McMaster*●, D.G. Dixon●, K.R. Munkittrick°, C. Portt·, G.J. Van Der Kraak■,
I.R. Smith' and D. Rokosh'

● Biology Dept., University of Waterloo, Waterloo, ONT., N2L 3G1.
° Fisheries and Oceans, Bayfield Institute, Burlington, ONT.
. C. Portt and Associates, Guelph, ONT., N1H 3H5.
■ Zoology Dept., University of Guelph, Guelph, ONT., N1H 3H5.
' Water Resources Branch, Ontario Ministry of Environment, Rexdale, ONT., M9W 5L1.

INTRODUCTION

The impact of bleached kraft pulp mills on aquatic ecosystems is a matter of international concern. Until recently, knowledge of the toxicity of pulp and paper mill effluents to aquatic life has been based primarily on laboratory toxicity tests performed under controlled conditions. Both the Canada Department of Fisheries and Oceans and the Ontario Ministry of Environment recently commissioned reviews of the impacts of pulp and paper mill effluents on aquatic life. There is a lack of knowledge of the influence of both untreated and treated whole mill effluents on the early developmental life stages of sensitive aquatic organisms, their reproduction and resistance to disease (Bonsor et al., 1988; McLeay, 1987 Colody and Sprague, 1989). Andersson et al. (1988) reported a survey of BKME impacts on perch (Perca fluviatilis) collected off the east coast of Sweden. Perch exposed to BKME exhibited physiological changes up to 8 to 10 km from the effluent disposal site. The major changes consisted of decreased gonad growth, increased liver size, a ten-fold increase in liver MFO activity, abnormal carbohydrate metabolism, changes in haematology and increased fin erosion. Although their investigation of physiological and biochemical impacts was extensive, the study neglected to tie the changes together and offer any mechanism to explain the impacts. The content, design and conclusions of the Scandinavian studies have been challenged (Colody and Sprague, 1989; Sprague, 1989). Our 1988 and 1989 collections parallel those of the Swedish studies (Munkittrick et al., 1989), and are the only North American results of this type to become public to date.

The primary objectives of our research were to evaluate the impact of BKME exposure on the growth and reproduction of white sucker as well as to examine relationships between changes in the endocrine system and liver MFO enzymes.

MATERIALS AND METHODS

Effluent from the pulp and paper mill at Terrace Bay, Ontario reaches Lake Superior at Jackfish Bay. Jackfish Bay is relatively isolated and provides an ideal situation to test for the impact of BKME on wild fish populations. White sucker were collected from the spawning runs in Sawmill Creek (Jackfish Bay) and the Little Gravel River (Mountain Bay), our reference site, by overnight hoop net sets in May, 1989. Fish were also collected during July and August by overnight gillnet sets in Jackfish and Mountain Bays as well as a second control site in August, Black Bay. Fork length and weight as well as the age of all fish were determined. A condition factor (k) was calculated for all fish as 100(weight/length^3). A liver somatic index was calculated as 100(liver weight/(total weight - liver weight)). A gonadosomatic index was calculated wherever possible as 100(gonad weight/(total weight - ovary weight)).

Reproductive Performance

Reproductive potential was assessed in spawning males by measuring milt volume, spermatocrit, spermatazoan motility and seminal plasma constituents. In prespawning females, reproducive potential was assessed by determining fecundity and egg size, in spawning females by determining their fertility, and in July females by estimating egg release. The effects of inherited contaminant burdens were assessed by the examination of larval responses and by cross-fertilization of gametes from exposed sites with reference gametes. Fertilized eggs were returned to the laboratory and evaluated for effects on survival, development, growth, behaviour, yolk absorption efficiency, deformation and initiation of exogenous feeding.

Relationships Between Endocrine and MFO Systems

Fish were sampled during prespawning, spawning and both summer periods for evaluation of circulating levels of steroids and liver MFO activity. Steroids were measured by radioimmunoassay by Dr. Glen Van Der Kraak using standard methods (Van Der Kraak et al., 1985; Van Der Kraak and Donaldson, 1986). MFO determinations were conducted by Ontario Ministry of Environment personnel.

In an attempt to identify the location of the impact of BKME on the endocrine system, white sucker were collected and caged in clean water. Fish received an injection of a principal gonadal steroid and circulating levels of the steroid were then to be monitored over time. This would allow assessment of pituitary function and steroid clearance rate from the blood. However, these attemps were unsuccessful due to high mortality at the control sites.

Significance to other Species

During the August sampling trip, preliminary work was completed on Lake Whitefish, which are a commercially important species in Lake Superior. Any incidental whitefish that were caught in the nets were weighed and measured. The gonads and the liver were also removed and weighed to allow site comparisons.

RESULTS

During all collections, male and female white sucker exhibited a decreased length and weight and a higher condition factor at the BKME site. This increased condition factor and an apparent increase in body fat were consistent with an increased water temperature at the BKME site, but were inconsistent with impacts on growth and reproduction. Both sexes exhibited a decreased growth rate and a shift in size distribution towards smaller fish.

Ripe male white sucker collected during the spring of 1989 showed decreased sperm motility, but no differences in milt volume, spermatocrit, or seminal plasma constituents (Na, K, Cl, osmolality). Female fish had a decreased egg size, a decreased GSI among older fish, and a decreased fecundity in younger fish. Egg size at the BKME site did not increase with age. There were no apparent differences in fertilization rates or in the females ability to release eggs between sites. Studies on eggs returned to the laboratory showed no differences in larval survival, development, behavior, or initiaion of exogenous feeding. However, the larvae do appear to grow at a slightly slower rate at the BKME site. During the August collections, male fish showed no secondary sexual characteristics (tubercles). All mature males examined in August at four other sites showed significant tubercle development.

Testosterone levels were significantly reduced in both prespawning and spawning females at the BKME site. Testosterone, 11-ketotestosterone and 17α,20ß-dihydroxyprogesterone levels were significantly reduced in exposed males during the prespawning and spawning periods. July samples showed no differences in female steroid levels, but males showed reduced levels of testosterone and 11-ketotestosterone. August samples showed reduced testosterone in both females and males relative to two reference sites, as well as reduced 11-ketotestosterone levels in males and reduced 17ß-estradiol levels in females.

The MFO analysis determined the activity of benzo(a)pyrene (BaP) hydroxylase (aryl hydrocarbon hydroxylase activity, AHH) towards diphenyloxazole (PPO) and BaP. Spawning male white sucker showed a 2- to 3-fold increase in activity for both BaP and PPO substrates. Spawning females did not show increased activity relative to the reference site. Summer collected white sucker showed a 6- to 18-fold increase in activity towards PPO, and 5-fold increase in BaP activity. There was no significant difference in UDPGT activity (glucuronosyl transferase activity towards p-nitrophenol) in the summer samples. The steroid injections attempted in August were unsuccessful. However, when BKME exposed fish were removed to clean water for a period of four days, there was a significant reduction in MFO activity (both PPO and BaP) when compared to the BKME site.

Preliminary work on the whitefish that were collected from under the plume, revealed marked elevations in body fat, decreased gonadal size and increased liver weight relative to those at two reference sites. A large number of the BKME fish showed no evidence of gonadal maturation two months prior to the spawning season.

DISCUSSION

Although condition factor increased at the BKME site, there was no concomitant increase in growth rate, suggesting that factors associated with energy allocation have been affected. Factors which might affect energy allocation include liver damage and/or decreased food availability. In females, the decreased growth rate and fecundity are characteristic of a population experiencing problems with food availability (Munkittrick and Dixon, 1989). However, white sucker show an increased condition factor. The combination of increased condition factor, decreased growth (length at age), and decreased fecundity observed at the BKME site appears paradoxical. Fish which cannot obtain sufficient energy for either growth or reproduction would be expected to show a lower condition factor. These results are consistent with the hypothesis of impacts of increased MFO activity on carbohydrate metabolism.

White sucker usually show an increase in egg size as they get older, as was noted at the reference site in this study. However, egg size did not increase with age at Jackfish. This was also noted in a previous study associated with the absence of the growth of mature fish (Munkittrick and Dixon, 1988), but at Jackfish the white sucker are continuing to grow, although at a decreased rate. The relative decrease in egg size of older fish results in a relative decrease in gonad weight, without a change in absolute fecundity. However, younger females at the Jackfish site show a decreased fecundity relative to the reference site. The correlations of fecundity changes with younger fish instead of older fish, and the increased condition factor at BKME sites suggests that the impact of BKME is not on food availability, but on the ability of the fish to convert the energy into growth or reproduction. These changes, along with the decreased gonadal size in males and the absence of secondary sexual characteristics, suggests that there are major abnormalities in the reproductive cycle. The decrease in steroid levels found throughout the year at the BKME site support this hypothesis. Despite the lower steroid levels (as much as 50% reduced), and the reduction in gonadal size, these fish still appear to spawn successfully as there were no differences in fertilization rate of the eggs, or survival, development, behavior, and initiation of exogenous feeding in the larvae.

One of the functions of the MFO system is to hydroxylate multi-ring carbon compounds to increase their solubility and facilitate their excretion. It has been suggested that the increased MFO activity associated with BKME exposure might affect circulating levels of hormonal steroids (Jonsson et al., 1976; Thomas, 1988), which have a multi-carbon ring nucleus, and are essential for the control of reproduction. The decreased steroid levels in our study also appear to be associated with the increase in MFO activity. We felt that these increased MFO activities were reducing the circulating levels of steroids in the blood. However, we were unsuccessful in our attempt to display this link between increased MFO activity and decreased steroid levels due to our inability in keeping caged suckers alive. However, when looked at on an individual basis, there was not a significant regression between MFO activity and steroid levels at the BKME site. For example, the fish with the highest induced MFO activity did not correspond to the fish with the lowest steroid levels. From these results, it becomes obvious that more work is needed before the critical links between BKME exposure, increased MFO activity and impacts on reproduction can be made.

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B13

INVOLVEMENT OF BILE DUCT DISEASE AND LOSS OF RESISTANCE TO CHEMICAL CARCINOGENS IN THE PATHOGENESIS OF LIVER NEOPLASMS IN BENTHIC FISH FROM LAKE ONTARIO

G.M. Kirby, P.J. Byrne, M.J. Stalker, I.R. Smith and M.A. Hayes

Department of Pathology, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

ABSTRACT

The relationship between hepatic neoplasia and concurrent parasitic liver disease was examined in white suckers from polluted regions of western Lake Ontario. Fluke *(Sanguinicola sp)* and nematode (Spirurida) liver infestation resulted in inflammation, fibrosis, bile duct proliferation, and subsequent biliary obstruction and cholestasis. Adult male white suckers with segmentally obstructed livers, identified by exploratory laparotomy, were orally administered ^{3}H-benzo(a)pyrene (^{3}H-BaP) (70 Ci/mmol; 2.5 mCi/fish). Cytosolic glutathione S-transferase (GST) activity (CDNB conjugation) in obstructed liver was approximately 50% of normal surrounding liver. Covalent binding of ^{3}H-BaP to hepatic protein was 1.5 fold greater in obstructed liver compared to corresponding normal liver. The formation of BaP-DNA adducts was minimal in both obstructed and normal liver (5 fmol/mg DNA), however one obstructed lobe had significantly higher levels of adducts (120 fmol/mg). The primary bile acid chenodeoxycholic acid (CDCA) represented 23% of total bile acids extracted from cholestatic liver and 5% of total in normal liver when analyzed by HPLC. Oral administration of CDCA (50 mg/fish) in white suckers resulted in a 33% decrease in cytosolic GST activity. CDCA inhibited cytosolic GST activity in vitro in a dose-related manner (I_{50}=100μM CDCA). Cholestasis resulting from parasitic liver disease alters the bile acid composition of white suckers resulting in a significant elevation in CDCA. CDCA is a potent inhibitor of GST, an important enzyme involved in the detoxification of PAHs in white suckers. Concurrent hepatic disease may increase the susceptibility of white suckers to hepatocarcinogenesis by reducing constitutive resistance to carcinogenic PAHs.

INTRODUCTION

Epidemiological evidence indicates that a complex interplay of etiologic and pathologic factors may be responsible for the development of liver cancer in many species (Harris and Sun, 1984; DeFlora et al., 1989; Lee et al., 1990;). Hepatocellular carcinoma (HCC) frequently coexists in conditions of dynamic hepatic disease in which inflammation, hepatocellular necrosis, proliferation and cirrhosis are commonly observed. In man, chronic liver disease, caused by a variety of parasitic (schistosomiasis, clonorchiasis, opisthorchiasis), viral (hepatitis B virus infection) and toxic (alcoholism, aflatoxicosis) agents is commonly associated with primary hepatocellular carcinoma (HCC) in high prevalence regions (sub-Saharan Africa and the Far East) (Nakashima et al 1975; Kew and Popper, 1984).

In western Lake Ontario, white suckers exposed to chemical carcinogens in contaminated sediment develop liver cancer that is frequently associated with inflammatory and proliferative liver disease, bile duct obstruction and cholestasis (Hayes et al., 1990). The association between concurrent liver disease and the development of liver neoplasms in white suckers indicates a multifactorial carcinogenic process involving chemical carcinogens as only one causative factor. We have attempted to characterize the mechanistic basis of multifactorial hepatocarcinogenesis in white suckers, to determine how concurrent liver disease might make these fish susceptible to environmental carcinogens such as polycyclic aromatic hydrocarbons (PAH).

Cholestasis is known to produce profound changes in bile acid metabolism which, in turn, may induce alternate pathways of xenobiotic metabolism. For example, GSTs have dual functions in the liver ie catabolism of xenobiotics and a binding/carrier function for endogenous substances that are not substrates (ie bilirubin and bile salts). Numerous experimental studies have demonstrated that, by acting as non-substrate ligands, high intracellular concentrations of bile acids have a strong inhibitory effect on GST activity (Boyer and Vessey, 1987; Singh et al., 1988; Boyer et al., 1984; Hayes and Mantle, 1986; Vessey and Zakim, 1981). Our previous studies have demonstrated that glutathione conjugation is an important means of detoxifying PAHs to which white suckers are exposed (Kirby et al., 1990). Concurrent cholangiohepatitis and cholestasis may render these fish more susceptible to PAHs by altering normal bile acid metabolism and inhibiting constitutive detoxification enzymes such as GST. In this study we have examined the effect of segmental cholestasis and bile acid accumulation on the metabolism and toxicity of BaP in white suckers.

MATERIALS AND METHODS

Materials.

Hydroxyapatite (DNA grade, Bio-Gel HTP) was obtained brom Bio-Rad Laboratories (Mississauga, Ont.). ^{3}H-BaP (specific activity 70 Ci/mmol was purchased from New England Nuclear (Boston, MA). Chenodeoxycholic acid (99% purity), deoxyribonuclease 1, alkaline phosphatase type III (EC 3.1.3.1) and phosphodiesterase I (EC 3.1.4.1) were purchased from Sigma Chemical Company (St. Louis, MO.)

Treatment of animals

Male white suckers (n=241) were caught from the Humber River (Toronto, Ontario) and Keefer's Creek (Owen Sound, Ont.) during their spring spawning migrations and were maintained for 1 week in laboratory holding tanks in clean well water. Laparotomies were performed on all fish under anesthetic (2-phenoxyethanol, 5ml/liter water) to examine for the presence of segmental liver obstructions. Fish were orally administered ^{3}H-BaP (70 Ci/mmol; 2.5 mCi/fish) and were killed 18 hours later. Obstructed and normal liver was separated and frozen for further analysis. In a separate experiment, CDCA (50 mg/fish) was administered by gavage followed in 2 hours by oral dosages of ^{3}H-BaP (2.5 mCi/fish). Fish were killed 18 hours later and liver samples were removed and frozen. Obstructed and normal liver was removed from untreated fish for preparation of cytosol and bile acid extraction.

Isolation of DNA and preparation of BaP-DNA adducts

BaP-modified DNA was isolated from normal and obstructed liver tissue by hydroxylapatite chromatography according to the method described by Adriaenssens et al. (1984). Briefly, tissues were homogenized in 0.16 M sodium phosphate containing 8 M urea (MUP) with EDTA, centrifuged and washed with ethyl acetate and diethyl ether. Following nitrogen evaporation of the organic solvents the aqueous layer was applied to hydroxylapatite columns (5 cm X 30 cm) and residual proteins and RNA were eluted with 0.24 MUP. After elution of urea with 0.48 M phosphate buffer, the DNA was eluted with 0.48 M phosphate buffer and was concentrated and dialysed against 10 mM Tris-HCl/$MgCl_2$ buffer (pH 7.1) in an Amicon model 52 concentrator apparatus with a YM10 membrane. The DNA was then precipitated with 2 volumes of ethanol, redissolved in 1 ml 10 mM Tris-HCl/$MgCl_2$ and quantified by 260 nm absorbance . BaP-modified DNA was hydrolyzed to deoxyribonucleosides according to a method described by Alexandrov et al (1988). DNA (1 mg/ml buffer) was dissolved in 10 mM Tris-HCl/$MgCl_2$ buffer (pH 7.1) containing 10 mM MgCl and was enzymatically digested to nucleosides using DNase I (400 units/mg DNA) for 8 hours; phosphodiesterase (0.06 units/mg DNA) for 48 hours and finally alkaline phosphatase (2.5 units/mg DNA) for 24 hours. Nucleosides bound to DNA were separated from free nucleosides by applying samples to Sep-Pak C18 cartridges, washing unbound nucleosides with 30% methanol and eluting BaP-nucleoside adducts with 80% methanol. Radioactivity was then assessed by LSC and expressed as fmol/mg DNA.

Protein isolation and quantification of BaP covalently bound to protein

Protein was isolated from the CIP extract obtained during the isolation of DNA as described by Stowers and Anderson (1984). Briefly, 1 ml aliquots of each CIP extract were shaken, centrifuged and the protein was then exhaustively washed with methanol, ethyl acetate and finally 90% methanol until counts were at background levels. Pellets were dissolved in 2 ml 0.5 N NaOH and radioactivity was analysed by liquid scintillation chromatography and expressed per unit protein.

Extraction and HPLC analysis of bile acids

Bile acids were extracted from obstructed and normal liver tissue according to a method developed by Kinugasa et al, 1981. Briefly, whole liver pooled from obstructed and normal lobes were homogenized in 2 volumes of distilled water and lyophilized. Samples (1g) were then extracted overnight in 100 ml ethanol containing 0.1% ammonia. The extracts were evaporated to dryness, dissolved in 70% methanol and neutral lipids were removed twice with n-hexane. The 70% methanol layer was then evaporated to dryness, dissolved in distilled water and aqueous components were removed by loading the sample onto Sep-Pak C18 cartridges, washing with distilled water, and eluting bile acids in methanol for HPLC analysis. Individual bile acids were separated by reverse phase HPLC on a C18 column (Biorad Hipore RP-318; 250 x 4.6 mm) with a continuous gradient flow of 40 mM ammonium phosphate buffer (solvent A) and acetonitrile (solvent B) (initial 35% A; 65% B, final 40%A; 60% B) in thirty minutes at a flow rate of 1.25 ml/min. Individual bile acids were detected by UV absorbance (210 nm) and were identified by bile acid standards in methanol and quantified by integration of peak areas.

Chenodeoxycholic acid inhibition of GST activity

Samples of liver were homogenized in 0.25 M cold sucrose (containing 5 mM HEPES, pH 7.0). Cytosol was prepared as the final supernatant of centrifugation at 10,000g (30 min, 4^oC) and 100,000 g (60 min 4^oC). Cytosolic GST activity was determined with 1-chloro-2,4-dinitrobenzene (CDNB) as substrate (pH 6.5, 25^oC) by the method of Habig *et al*., (1974). Protein concentrations in cytosol were determined by the Biorad protein assay. The inhibitory effect of chenodeoxycholate on the GST-mediated conjugation of glutathione to CDNB was measured by preincubating the sample with five different concentrations (100, 200, 300, 400 and 500 mM) of the inhibitor for 30 minutes prior to administration of the substrate. Because of the limited solubility of chenodeoxycholate, 1.25% (v/v) methanol was included in each assay, including controls.

RESULTS

Segmental liver obstructions were visible as caudal liver lobes discolored dark green with retained bile pigments in 14% of male white suckers from the polluted site (Humber R.) (Table 1). No obstructions were visible grossly in reference fish. Tumors were visible grossly as focal areas of discoloration (tan brown color) or as large raised neoplasms frequently within or in close assocation to obstructed lobes. Histologically, there was periportal fibrosis, necrosis of bile duct epithelium, infiltration of melanomacrophages and other inflammatory cells, retention of bile pigments, and bile duct proliferation within these obstructed areas (Fig. 1). Trematodes *(Sanguincola sp.)* and nematodes (Spirurida) were visible within bile ducts and migrating through liver parenchyma. (Fig.1). Foci of hepatocellular and cholangiocellular alteration and advanced neoplasms (cholangiocellular and hepatocellular carcinoma were frequently adjacent to areas of bile duct inflammation and fibrosis (Fig. 2).

Cytosolic GST activity in segmentally obstructed cholestatic lobes was 63% of the GST activity normal liver. BaP-deoxyribonucleoside adducts and BaP adducted to hepatic protein was higher in obstructed liver compared to normal liver (Table 2, Fig. 4). HPLC analysis of extracted bile acids revealed that the primary bile acid chenodeoxycholic acid (CDCA) was elevated approximately 6 fold in cholestatic liver (Fig. 5) in comparison to normal (Fig. 6) and represented 23 mole % of total bile acids (Table 3).

Hepatic cytosolic GST activity in suckers treated orally with chenodexycholic acid was 66% the GST activity of control fish (Fig 7.). The inhibition of hepatic cytosolic GST by CDCA in vitro was dose-related in μmolar concentrations (I_{50}=100 μM).

DISCUSSION

This study indicates that concurrent hepatic diease in white suckers is associated with a reduction in constitutive resistance to carcinogenic PAHs. In spite of the correlation between HCC and hepatic disease, there is little experimental evidence concerning the cellular and molecular mechanisms involved in hepatocarcinogenesis (Gu, 1988). While it is well recognized that neoplasia is a consequence of persistent hepatocellular proliferation, it is equally conceivable that altered xenobiotic metabolism in hepatitis and cirrhosis increases the susceptibility of hepatocytes that are normally resistant to chemical hepatocarcinogens. For example, recent studies indicate that stimulation of carcinogen metabolism in hepatitis B virus-infected woodchucks may be an important factor in the synergism of viral hepatitis and HCC.

During cholestasis, the intracellular concentration of organic ions such as bile acids increase to levels which significantly impair the catalytic activity of GST (Greim et al., 1972; Boyer and Vessey, 1987). This suggests that cholestatic liver may be unusually susceptible to injury by toxic electrophiles detoxified by GST. Cholestasis in several species, including humans, usually results in a reduction in secondary and tertiary bile acids and a shift towards increased primary bile acids such as cholic acid and chenodeoxycholic acid (Oelberg and Lester, 1986; Palmer R.H., 1972; Kinugasa et al., 1981; Greim et al., 1972; Greim and Popper, 1971; Greim et al., 1972). The bile acid composition of white suckers in this study closely resembles that of rainbow trout (Denton and Yousef, 1974). For example, CDCA comprises approximately 5% of total bile acids of normal adult fish of both species. The increase in CDCA (24% of total bile acids) in cholestasic liver of white suckers has also been observed in rats with bile duct ligation (Kinugasa et al., 1981; Greim et al., 1972; Greim and Popper, 1971) and severe chronic biliary obstruction in humans (Greim et al., 1972). Concentrations of CDCA less than 100 μM, levels that correspond to intrahepatic concentrations during cholestasis, (Greim et al., 1972) are strongly inhibitory for most rat hepatic GST isoenzymes in vitro (Hayes and Mantle., 1986). Because GSH conjugation diminishes the binding of PAH epoxide metabolites to DNA (Hesse et al., 1982; Hesse et al., 1990; Jernstrom et al., 1982; Ketterer, 1988), a reduction in GST activity may increase the susceptibility of DNA to electrophilic attack. Therefore, the inhibition of GST by CDCA both in vivo and in vitro and the increased toxicity of BaP in obstructed liver suggests that the altered bile acid compositon in cholestatic liver may reduce GST-mediated resistance to PAHs in white suckers.

It is interesting to speculate on possible mechanisms that might explain the differences in susceptiblility of these fish and other species to hepatocarcinogenesis. Differences in susceptibility to hepatocarcinogenesis may indeed be related to liver disease and changes in bile acid metabolism. For example, experimental studies have demonstrated a promotional effect of bile duct obstruction and various bile acids in hepatocarcinogenesis (Kinami et al., 1990; Blair et al., 1990; Kitazawa S. et al., 1990; Cameron R.G. et al., 1982; Tsuda et al., 1984; Tsuda et al., 1988). Furthermore, experimentally-induced postnecrotic cirrhosis (Watanabe et al., 1987; Newberne et al., 1966) and fluke infestation (Thamavit et al., 1987; Thamavit et al., 1988) are important promoting factors in chemical hepatocarcinogenesis. Others have suggested that the relationship of bile acids to liver tumor development may be due to intrinsic mutagenic/initiating activity of bile acids, (Kitazawa et al., 1990), metabolic formation of carcinogenic metabolites from bile acids (Cook and Hasslewood, 1934), and hepatocellular injury due to detergent effects of bile acids (Greim et al., 1972).

The phenomenon of parasite-induced liver disease and the relationship to hepatic neoplasia in white suckers may be contextual and related to environmental conditions. For example, sanguinicolids are usually found in blood vessels (ie. mesenteric arteries) of fresh water fish with lodging of eggs terminally in gill lamellae. It is unusual for adult sanguinicolids to migrate to the liver and even rarer for adults to be found within bile ducts. It is possible that this anomalous trematode migration is due to heavy infestations resulting from conditions associated with polluted environments that may influenceß the life cycle of Sanguinicola sp. (ie. higher concentrations of snail intermediate hosts). The fact that relatively few flukes were extracted from obstructed liver may be due to seasonal fluctuations in sanguinicolid infestation a hypothesis that is supported by extraction of immature forms in this study. However, the inflammatory reaction within the liver is likely an immune response to deposited eggs and totally unrelated to the mechanical presence of adults. Similarly, the presence of the spirurid nematode within the liver (tentatively identified as Acuraridoidea) is also considered unusual. Interestingly, the definitive host of acuarids is usually a piscivorous bird, such as gulls, which are becoming increasingly prevalent in industrialized areas. It is likely, therefore, that the hepatic disease concurrent with liver neoplasia is a species specific phenomen in white suckers (eg. species specific parasites, liver anatomy etc) and not readily extrapolated to humans. Nevertheless, parallels may be drawn in similar situations in humans where loss of constitutive resistance (ie. elderly patients, chronic alcoholism, hereditary anomalies of xenobiotic metabolism) increases the susceptibility to liver neoplasia.

The low liver tumor incidence in white suckers exposed to high sediment levels of PAHs (Hayes et al., 1990), the detoxification of reactive intermediate metabolites of PAHs by GSTs (Kirby et al., 1990) and the low levels of BaP-DNA adducts observed in this study suggest that these fish are normally quite resistant to the carcinogenic effects PAHs. Alterations to the mechanisms that provide this carcinogenic resistance (ie. reduction in GST activity) may explain any increase in susceptibility. The coincidence of liver disease and hepatic neoplasia and the reduced detoxification of carcinogens associated with cholestasis in these fish suggest that there is a strong association between the consequences of hepatic disease and loss of resistance to PAHs in white suckers.

TABLES

Table1. Prevalence of segmental liver obstructions in white suckers from polluted and reference sites.

Site	Number of fish	Number with segmental obstructions	% of total
Humber R.[1]	241	33	13.6
Keefer's Cr.[2]	36	0	0

[1] Toronto, Ont., polluted site

[2] Owen Sound, Ont., reference site

Table 2. Quantification of BaP-deoxyribonucleoside and BaP protein adducts in cholestatic and normal liver from white suckers.

	BaP-DNA adducts (fmol/mg DNA)				BaP-protein adducts (fmol/mg protein)			
	fish no.				fish no.			
Type of liver	1	2	3	4	1	2	3	4
normal	2.7	20.5	6.3	2.3	3	12	8	6
cholestatic	133.3	1.1	1.7	0.5	20	13	4	4

Table 3. Comparison of distribution of chenodeoxycholic acid in cholestatic and normal liver from white suckers

Bile Acids	Normal liver	Obstructed liver
Total bile acid pool (mmol/g tissue)	2.5	2.9
CDCA (μmol/g tissue)	120	690
CDCA (mole % total)	5	23

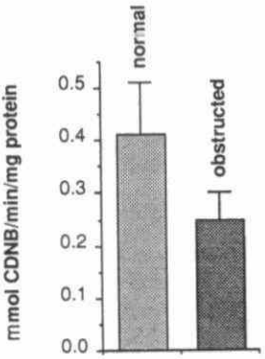

Fig 3. Cytosol GST activity in cholestatic and normal liver of tissue white suckers

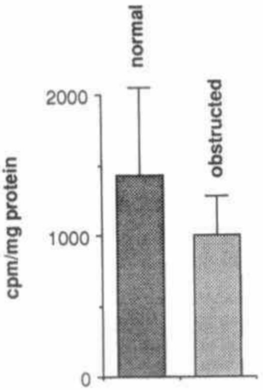

Fig 4. Covalent binding of ^{3}H-BaP to hepatic protein in cholestatic and normal liver of white suckers

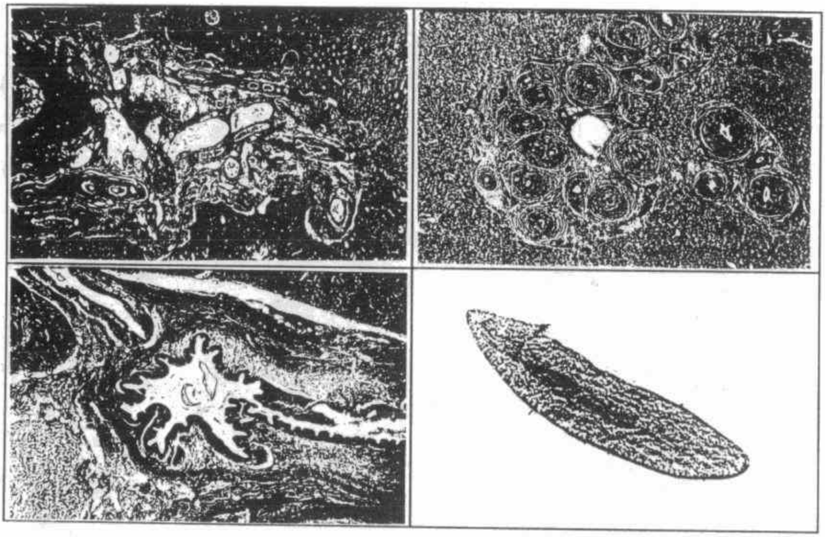

Fig. 1. Parasitic bile duct disease in white sucker liver. a, Cholangiohepatitis, periportal fibrosis and bile duct proliferation. b, Proliferative bile ducts. c, *Sanguinicola sp.* present in major bile duct with periductal fibrosis. d, *Sanguinicola sp.* extracted from obstructed liver lobe.

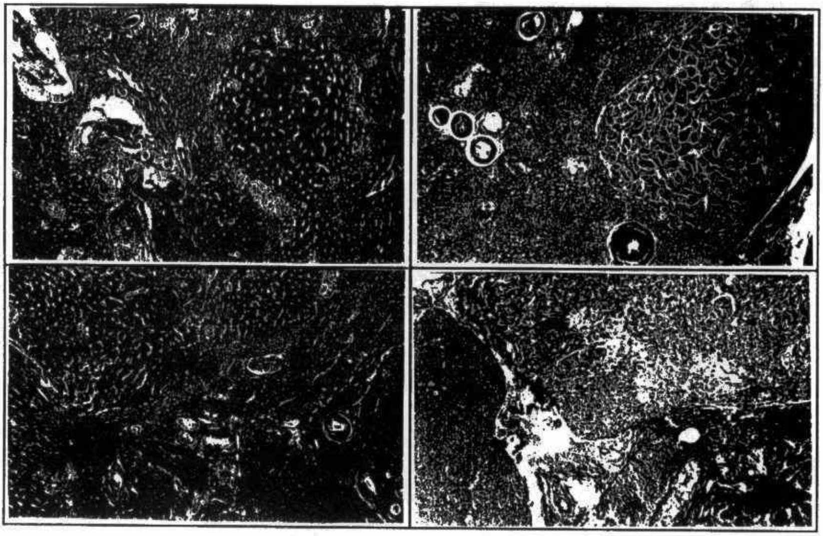

Fig. 2. Hepatic neoplasia in association with bile duct disease. a, Focus of hepatocellular alteration and bile duct inflammation. b, Cholangioma with adjacent parasitic granulomas. c, Hepatocellular carcinoma and d, cholangiocellular carcinoma adjacent to areas of bile duct fibrosis and proliferation.

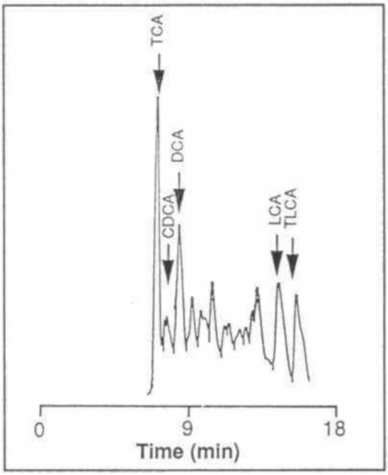

Fig.5. Chromatogram of bile acids extracted from normal liver

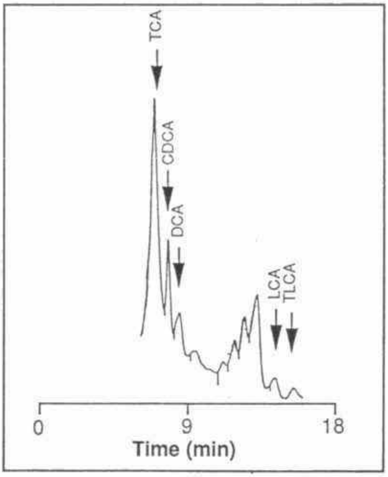

Fig. 6. Chromatogram of bile acids extracted from obstructed liver showing increase in CDCA.

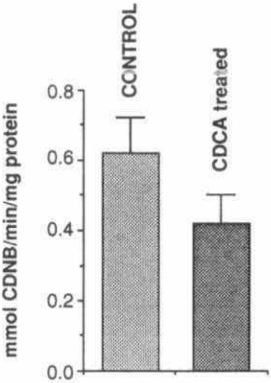

Fig. 7. Hepatic cytosolic GST activity in suckers treated orally with chenodeoxycholic acid and controls.

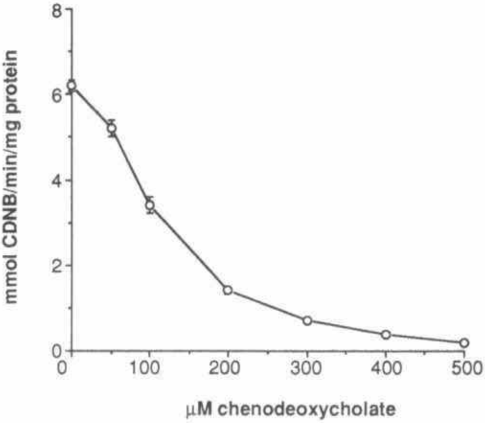

Fig. 8. Inhibition of sucker hepatic cytosolic GST by chenodeoxycholic acid in vitro.

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B14

The use of Benthic invertebrates in mapping toxic areas of sediment and determining the efficacy of sediment cleanup operations

by

Mike Dickman[1], Frances Fiore[1] and Ian Brindle[2]

1. Biological Sciences Department
Brock University, St. Catharines, Ontario, L2S 3A1
2. Chemistry Department
Brock University, St. Catharines, Ontario, L2S 3A1

Abstract

Chironomids are representatives of a widely distributed group of insects known as midges. Chironomids from 4 locations in the Niagara River Watershed were sampled and classified as either normal or deformed. Among the 230 chironomids taken from the contaminated site in 1988, 14% (32) possessed menta with gross deformities. Following the replacement of the contaminated sediments at this site with clean sediments, the frequency of menta abnormalities fell to 7% (n=176). The frequency of abnormalities at the upstream "control" site ranged between 2 and 11%. We concluded that the sediments in the "cleanup" area had been decontaminated and that in the absence of the coal tar contaminants (e.g. PAH's) the frequency of larval chironomid abnormalities declined to well within the background levels observed at the upstream control site.

Nickel, chromium, zinc and lead were 60 to 500 times more concentrated in the sediments downstream of the Atlas Specialty Steels Co. than they were in the sediments of the upper Welland River or in the Chippawa Creek. These metals reached concentrations of 4,900 mg kg^{-1} dry weight (ppm) of nickel versus 10 ppm upstream, 890 versus 5 ppm lead, 1,050 versus 30 ppm zinc and 5,120 verses 10 ppm chromium. Twenty five percent of the chironomids removed from the heavy metal contaminated sediments downstream of the Atlas Specialty Steels Co. Ltd. displayed gross mentum abnormalities. Further downstream, below the Welland Sewage Treatment Plant, the frequency of abnortmalities fell to 17 %. Both of these sites displayed significantly more deformed chironomids than at the control site ($P < 0.01$).

INTRODUCTION

Deformities of Benthic Invertebrates Exposed to Teratogens

Aquatic communities are logical places to study the impact of mutagens and teratogens. As a result, many ecologists have attempted to use invertebrate deformities to indicate the presence of genotoxins in aquatic sediments (Hamilton and Saether, 1971; Wiederholm, 1984; Warwick et al., 1987; Warwick, 1985 and Dickman et al. 1991). Research that was carried out on the frequency of deformities of chironomid larvae in polluted freshwater sediments led to the use of abnormalites in their mouth parts (menta), and antennae as a correlate with the presence of genotoxic contaminants (Hamilton and Saether, 1971; Wiederholm, 1984; Warwick et al., 1987 and Lan et al. 1990).

The most widely distributed benthic invertebrates in freshwater are Chironomid larvae. These larvae represent one of the more sensitive stages in the Chironomid life cycle. Chironomid larvae have symmetrical mouth parts (menta). Deformed specimens are characterized by menta which are asymmetrical. Hamilton and Saether (1971) also considered unusual thickening of the chironomid larval body wall as a deformity. These researchers have also suggested that different types of deformities may be induced by different types of pollutants. For example, certain types of chemicals are associated with an unusually high frequency of deformed antennae (Warwick et al. 1987), while other chemicals are associated with an unusually high frequency of deformed mouth parts (Dickman et al. 1990). This susceptibility to various pollutants appears to also differ among distinct chironomid species (Wiederholm, 1984). Warwick et al. (1987) also found that some chironomid species are far more sensitive to mutagens than are other species.

Tradescantia

Tradescantia, more commonly known as Spiderwort, is a perennial herbaceous plant that can be affected by radiation and certain chemical mutagens (Cebulska-Wasilewska et. al, 1981). It is a plant that readily propagates asexually and one that flowers continuously throughout the year. *Tradescantia* is quite suitable for both laboratory and in situ studies and as a result it is a commonly utilized scientific subject (Ichikawa, 1981).

Tests that most commonly employ the Spiderwort include two mutagenicity assays; the stamen hair assay and the micronucleus assay. The stamen hair assay focuses on detecting all pink or clear mutant cells from the string of violet coloured cells that are normally present (Ichikawa, 1981). The micronucleus test is based on the principle that chromosome breakage caused by mutagens in the early meiotic pollen mother cells of *Tradescantia* occur as small additional nuclei (micronuclei or MCN). These MCN are revealed in the cells of tetrads which are the end products of meiosis (Te-Hsiu, et al., 1983).

Objectives of this Study

The purpose of this study was to determine whether the sediment clean up operation at a site on the Niagara River (Chippawa) had resulted in a statistically significant reduction in the number of chironomid abnormalities occurring at the site prior to the clean up. The second objective of the study was to determine whether or not a positive correlation occurred between the responses of freshwater benthic invertebrates of the family Chironomidae and the angiosperm, *Tradescantia* as indicators of the presence of genotoxins in the sediments of aquatic environments. The frequency of chironomid mentum deformities and the frequency of irregular mutational events that occurred in *Tradescantia* were compared to determine whether sediments associated with a high frequency of chironomid abnormalities would also induce a high frequency of pink events and micronucleus abnormalities in *Tradescantia*.

Data were compiled from four locations within the Niagara Watershed. Two sites were located in the City of Welland along the Welland River near the Atlas Specialty Steels Co. and two sites were situated along the same river in a small town known as Chippawa. The water at the latter two sites was Niagara River water and not Welland River water (Fig. 1).

Site Descriptions

Welland River at Atlas Steels - Upstream of the Welland STP

This sample site was situated 600m downstream of the Atlas-Mansfield discharge pipe and approximately 200m upstream of a Regional Niagara Sewage Treatment Plant (STP, Fig. 2). A total of 16 dredge samples were collected at this location from May 28 to July 8, 1990. Quite often an oily film could be seen on the water's surface immediately following any disturbance of the submersed sediments. Normally, samples were taken at a distance of about 1.5m from shore and at a depth of 0.5m. Various organisms were obtained during the sorting process however, only the chironomids were examined for this report.

Welland River at Club Richelieu

Club Richelieu, located on the Welland River just downstream of the Welland sewage treatment plant (Fig. 2) was sampled throughout the summer of 1990. Sediments removed from this site were known to have elevated levels of heavy metals and oily wastes.

This site is densely colonized by cattails and other aquatic vegetation which separate the shore from the river by about 100m. A total of 12 Ponar dredge samples were taken from July 30 to August 2, 1990 from the river in front of the cattail fringe at this site. Samples were taken in the cattail colonized area approximately 10m from the river's edge and at a water depth of approximately 0.6m. During the sampling process, an oily film formed on the water's surface and the sediments taken with the Ponar dredge oozed oiled as they were examined in the sorting tray.

Upper Niagara River at the Kane Dock (Chippawa Creek)

The water at this site (Fig. 1) flows from Lake Erie by way of the Niagara River. The sample area was located in the Village of Chippawa, between 4069 and 4083 Front Street, less than 50 m downstream of the Norton Abrasives Co. discharge pipe. A total of 8 ponar dredge samples were collected at this site from June 22 to July 3, 1990.

Upper Niagara River at Kingsbridge Park (Chippawa Creek)

The water at this site (Fig. 1) also comes from Lake Erie via the Niagara River. Kingsbridge Park is located about 800m upstream of the Norton Abrasives' outfall pipe and has been characterized as a "control site" in previous studies (Dickman et al. 1990). A total of 11 Ponar dredge samples were taken at this site from July 3 to July 19, 1990, yielding an abundant collection of chironomids and a variety of other aquatic organisms.

METHODS

Benthic Invertebrates

Sampling Procedure

Sediment samples were taken using a standard 15cm X 15cm Ponar dredge at each of the four study sites. The 10 kg Ponar penetrated the sediment to a depth of about four centimeters allowing the various organisms, particularly the benthic invertebrates dwelling within this region, to be collected in a quantitative manner. At least thirty chironomid larvae were obtained from each site. This number ensured that proper statistical analyses could be carried out.

All samples were transferred from the Ponar into a bucket containing a 0.75mm mesh sieve at its base. The contents in the bucket were then sieved thoroughly to ensure that a substantial proportion of the excess dirt and clay was removed from the sample. This practice greatly facilitated the quantitative removal of the chironomids during the sorting process. Each sieved sample was placed in a glass container and labelled.

Sorting was completed within a three day period for samples that were kept refrigerated and within twenty four hours of the sampling date for those which were not. Sorting and head capsule mounting procedures are detailed in Dickman et al. (1990).

Tradescantia

This portion of the study was carried out in the lab of Dr. Mike Salamone of the Ontario Ministry of the Environment in Toronto, Ontario.

Plant cuttings were obtained from the York University greenhouse and transported to the laboratory at the Ministry of the Environment. Approximately 30 cuttings were chosen per treatment. These cuttings were suspended in the sediment or control solution through perforated aluminum covers on disposable beakers for 24 hours. This ensured that liquid absorption through the stem would take place. Following exposure, the cuttings were thoroughly rinsed three times, twice with Hoagland's Nutrient solution and once with water. This practice reduced surface mutagen residue and, consequently, the hazard of handling contaminated plants.

Plants that were exposed only to Hoagland's Nutrient solution were used to establish a base-line control value. This group was kept in a separate fume hood to prevent gaseous contamination from chemical test solutions. The standard methods of Ichikawa, (1981, stamen hairs), and Te-Hsiu, et al.(micronuclei preparations) Te-Hsiu, et al. (1983) were followed with modifications described by Salamone (unpublished MOE report).

RESULTS

Tables 1-4 summarize the results of the 51 Ponar dredge samples taken from the 4 locations along Chippawa Creek and the Welland River between May 28 and August 2, 1990. Table 5 summarizes the results of the *Tradescantia* stamen hair and micronuclei assays which were carried out using sediment from the four above mentioned sample locations.

TABLE 1
Chironomid Data
Welland River at Kingsbridge, Chippawa

Chironomid Genera	Number of ind.	Number normal chiron.		Number of grossly deformed chironomids		Number dredge samples	Density (#/m^2)	Date sampled
		#	%	#	%			
Dicrotendipes	19	18	95%	1	5%	7	121	7/3/90
Chironomus Sp.	8	7	88%	1	12%	7	51	7/3/90
Crypto-chironomus	1	1	100%	0	0%	7	6	7/3/90
C. anthracinus	5	5	100%	0	0%	7	32	7/3/90
C. semi-reducuts	2	2	100%	0	0%	0	13	7/3/90
C. semi- reductus	68	60	88%	8	12%	4	833	7/19/90
Paratendipes	4	3	75%	1	25%	4	44	7/19/90
Polypedilum	1	1	100%	0	0%	4	11	7/19/90
Procladius	2	2	100%	0	0%	4	13	7/19/90
Totals	**110**	99	90%	11	10%	**11**	**698**	

Total No. Species = 8, Generic Diversity = 1.07

TABLE 2 Welland River at Kane Dock, Chippawa

Chironomid Genera	Number of ind.	Number of normal chironomids		Number of deformed chironomids		Number dredge samples	Density (#/m^2)	Date Sampled
		#	%	#	%			
Chironomus Sp.	2	2	100%	0	0%	4	22	6/22/90
Cryptochironomus	1	1	100%	0	0%	4	11	6/22/90
Cryptochironomus	2	2	100%	0	0%	4	22	7/3/90
Cryptochironomus	5	5	100%	0	0%	4	55	7/8/90
Dicrotendipes	2	2	100%	0	0%	4	22	7/3/90
Dicrtotendipes	2	1	50%	1	50%	4	22	7/8/90
Endochironomus	1	1	100%	0	0%	4	11	6/22/90
Endochironomus	5	5	100%	0	0%	4	55	7/3/90
Endochironomus	7	6	86%	1	14%	4	78	7/8/90
Orthocladius	2	2	100%	0	0%	4	22	6/22/90
Paratendipes	4	4	100%	0	0%	4	44	6/22/90
Paratendipes	3	3	100%	0	0%	4	33	7/3/90
Polypedilum	1	1	100%	0	0%	4	11	6/22/90
Procladius	2	2	100%	0	0%	4	22	6/22/90
Psectrocladius	2	2	100%	0	0%	4	22	6/22/90
Psectrocladius	1	1	100%	0	0%	4	11	7/3/90
Tanytarsus	1	1	100%	0	0%	4	11	6/22/90
Tribelos jucun.	1	0	0%	1	100%	4	11	6/22/90
Totals	**44**	**41**	**93%**	**3**	**7%**	**12**	**159**	

Total No. of Species = 11, Generic Diversity = 2.27

TABLE 3 Chironomid Data from Welland River at Club Richelieu

Chironomid Genera	Number of ind.	Number of normal chironomids		Number of deformed chironomids		Number dredge samples	Density (#/m^2)	Date sampled
		#	%	#	%			
Chaetocladius	1	0	0%	1	100%	6	7	8/02/90
Paratanytarsus	3	3	100%	0	0%	6	22	7/30/90
Paratanytarsus	9	8	89%	1	11%	6	67	8/02/90
Phenopsectra	1	1	100%	0	0%	6	7	8/02/90
Polypedilum	1	1	100%	0	0%	6	7	8/02/90
Procladius	2	1	50%	1	50%	6	15	7/30/90
Procladius	13	11	85%	2	15%	6	96	8/02/90
Totals	**30**	**25**	**83%**	**5**	**17%**	**12**	**111**	

Total No. of Species = 5, Generic Diversity = 1.48

TABLE 4

Atlas Steels Chironomid Data 1990
Welland River - Upstream of the Welland Sewage Treatment Plant

Chironomid Genera	Number of ind.	Number normal chironomids #	%	Number grossly deformed. chironomids #	%	Number dredge samples	Density (#/m^2)	Date sampled
Chaetocladius	1	1	100%	0	0%	4	11	5/28/90
Chironomus	1	1	100%	0	0%	4	11	5/28/90
Cladoplema	5	4	80%	1	20%	8	28	6/18/90
Cladopelma	2	1	50%	1	50%	4	22	7/08/90
Dicrotendipes	1	1	100%	0	0%	8	6	6/18/90
Paracladius	1	0	0%	1	100%	4	11	5/28/90
Paratendipes	1	0	0%	1	100%	8	6	6/18/90
Procladius	2	2	100%	0	0%	4	22	5/28/90
Tanypus	1	1	100%	0	0%	8	6	6/18/90
Tribelos	1	1	100%	0	0%	4	11	5/28/90
Totals	**16**	**12**	**75%**	**4**	**25%**	**16**	**44**	

Total No. of Species = 9

TABLE 5

Results 1990
Tradescantia Assays

Location of Sediment	Stamen Hair Assay	Micronucleus Assay
Kingsbridge #1	negative	negative
Kingsbridge #2	negative	negative
Welland Upstream STP #1	negative	neg/pos?
Welland Upstream STP #2	positive	neg/pos?
Garden Control	0	0
Kane Dock #1	negative	no data
Kane Dock #2	negative	negative?
Club Richelieu	negative	negative

The term "pos" is used to denote an increase over Garden Control or Kingsbridge, although the increase may not necessarily be significant.

Discussion

Kaiser and Combe (1983) described a number of types of volatile organic compounds that were found to exist in the industrial portions of the Welland River. Three of the compounds identified by Kaiser and Combe were genotoxic (Lan et al., 1990). In addition, chromium and nickel, both genotoxic heavy metals, were found at concentrations of about two orders of magnitude above background levels downstream of the Atlas Specialty Steels Co. (Dickman et al. 1991). It can be assumed therefore that the increased incidence of chironomid mentum deformities at both Club Richelieu and downstream of the Atlas Specialty Steels Co. (upstream of the Welland Sewage Treatment Plant) may be a direct result of the elevated concentrations of mutagenic heavy metal levels at these two locations.

In 1986, the Chippawa Creek, Kane Dock site was designated by the M.O.E. for a "cleanup" of its coal tar contaminated sediments. Experimental studies by Cushman (1984) indicated that pollution by a synthetic, coal tar-derived oil was correlated with a high frequency of mentum deformities in *Chironomus decorus* living in the contaminated sediments of his study ponds. We hypothesized that a cleanup of the PAH coal tar contaminated sediments in the Kane Dock area should therefore directly act to reduce the incidence of mentum deformities in chironomids sampled at this site. As indicated (Table 2), this hypothesis was supported by the fact that in 1990, 44 chironomids were removed from the cleanup site and only 7% displayed abnormalities. Before the cleanup, the frequency of abnormalities was 18% (Dickman et al. 1990). Ten percent of the 110 chironomids sampled at the control site (Table 1) displayed abnormal menta (Table 1).

Whether or not a correlation between the incidence of mentum deformities in chironomids and the mutational events that occur in *Tradescantia* exists could not be determined because, according to Dr. Salamone, the *Tradescantia* data (Table 5) were inconclusive. Although it appears as though the study site with the highest frequency of chironomid mentum abnormalities was also the site with the highest number of *Tradescantia* "pink events" additional testing with the *Tradescantia* will be needed to confirm these results.

Among the 230 chironomids taken from the contaminated site in 1988, 14% (32) possessed menta with gross deformities. Following the replacement of the contaminated sediments at this site with clean sediments, the frequency of menta abnormalities fell to 7% (n=176). The frequency of abnormalities at the upstream "control" site ranged between 2 and 11%. We concluded that the sediments in the "cleanup" area had been decontaminated and that in the absence of the coal tar contaminants (e.g. PAH's) the frequency of larval chironomid abnormalities declined to well within the background levels observed at the upstream control site.

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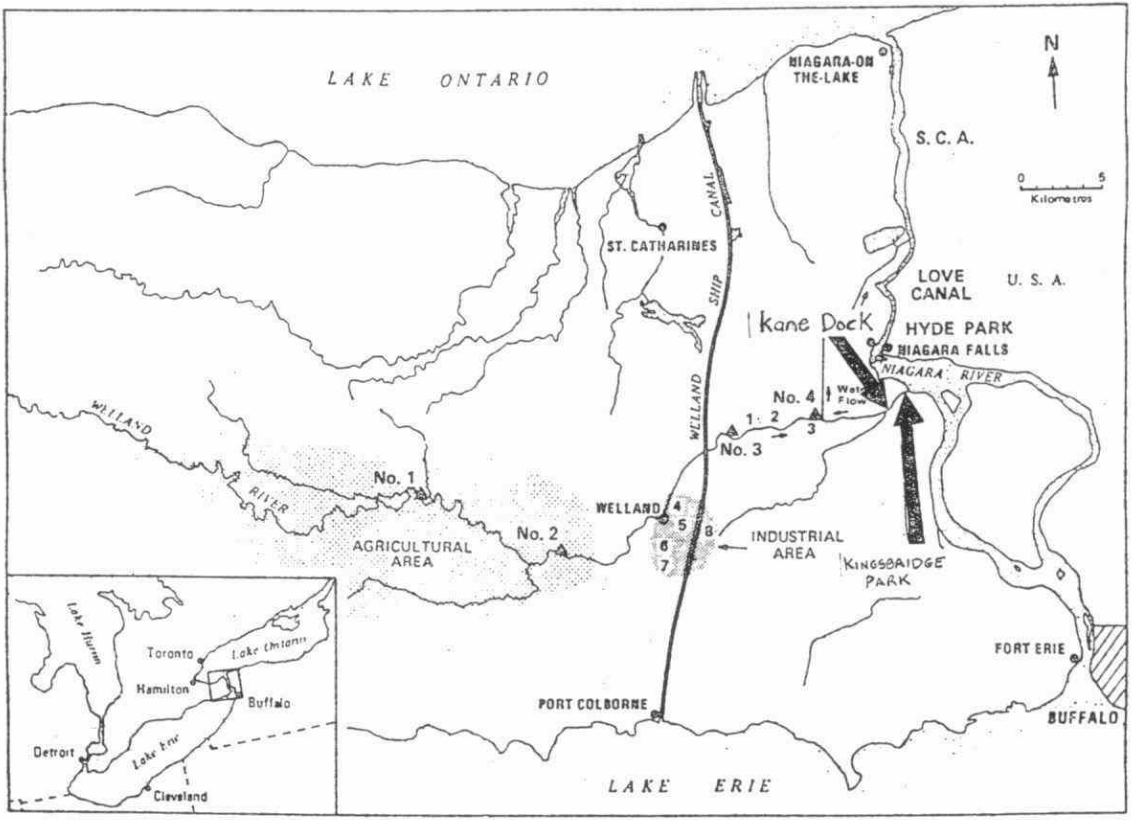
Figure Captions

Figure 1. The two study sites situated along the Chippawa River in Chippawa, Ontario are indicated by the arrows. The Atlas Specialty Steels and Club Richelieu sites are located near no. 4 in the Welland Industrial area. The inset indicates the location of the study area within the Great Lakes Region.

Figure 2. The two study sites situated along the Welland River in Welland, Ontario. Distances denote down stream measurements from the Atlas Specialty Steels discharge pipe. This figure was modified from a figure prepared for an MOE public document by Acres Consulting Ltd.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LOVE CANAL
U. S. A.
Kane Dock
HYDE PARK
NIAGARA FALLS
NIAGARA RIVER
No. 4
Water Flow
1 2
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No. 3
WELLAND RIVER
No. 1
WELLAND
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5
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7
8
No. 2
AGRICULTURAL AREA
INDUSTRIAL AREA
KINGSBRIDGE PARK
FORT ERIE
BUFFALO
PORT COLBORNE
LAKE ERIE
Lake Huron
Toronto
Lake Ontario
Hamilton
Buffalo
Detroit
Lake Erie
Cleveland

Figure 1

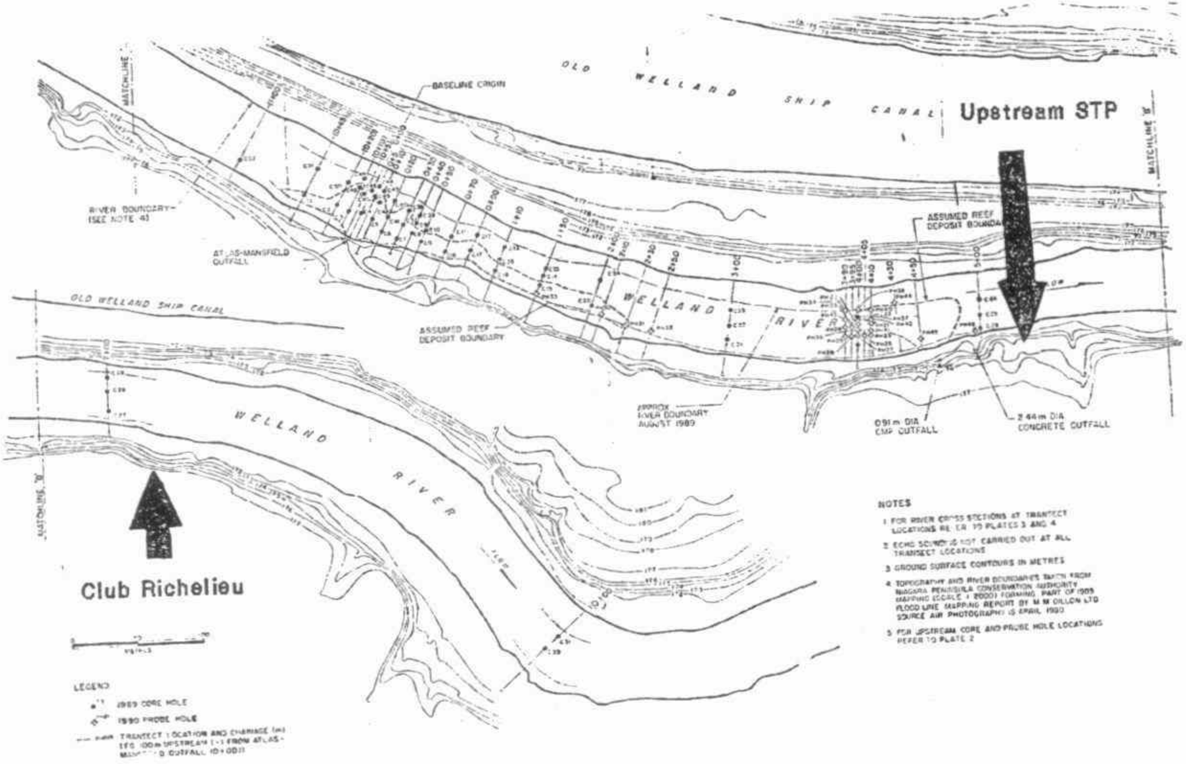
OLD WELLAND SHIP CANAL
Upstream STP
MATCHLINE 'B'
MATCHLINE 'A'
BASELINE ORIGIN
RIVER BOUNDARY (SEE NOTE 4)
ATLAS-MANSFIELD OUTFALL
ASSUMED REEF DEPOSIT BOUNDARY
WELLAND RIVER
APPROX RIVER BOUNDARY AUGUST 1989
0.91 m DIA CMP OUTFALL
2.44 m DIA CONCRETE OUTFALL
OLD WELLAND SHIP CANAL
WELLAND RIVER
Club Richelieu
METRES
LEGEND
1989 CORE HOLE
1990 PROBE HOLE
TRANSECT LOCATION AND CHAINAGE (m) (E.G. 100 m UPSTREAM (-) FROM ATLAS-MANSFIELD OUTFALL (0+00))
NOTES
1 FOR RIVER CROSS SECTIONS AT TRANSECT LOCATIONS REFER TO PLATES 3 AND 4
2 ECHO SOUNDING NOT CARRIED OUT AT ALL TRANSECT LOCATIONS
3 GROUND SURFACE CONTOURS IN METRES
4 TOPOGRAPHY AND RIVER BOUNDARIES TAKEN FROM NIAGARA PENINSULA CONSERVATION AUTHORITY MAPPING (SCALE 1:2000) FORMING PART OF 1985 FLOOD LINE MAPPING REPORT BY M M DILLON LTD SOURCE AIR PHOTOGRAPHY IS APRIL 1980
5 FOR UPSTREAM CORE AND PROBE HOLE LOCATIONS REFER TO PLATE 2

Figure 2

B15

MONITORING OF ORGANIC CONTAMINANTS IN AQUATIC FOOD-CHAINS

G. Douglas Haffner*, Frank A.P.C. Gobas, Rodica Lazar, Diane Laviolet;
The Great Lakes Institute, University of Windsor, Windsor, Ontario, N9B 3P4

Research at the Great Lakes Institute of the University of Windsor is directed to assist government and industry in the environmental management of contaminants. This includes providing tools and protocols for monitoring of contaminants in the Great Lakes. To accomplish these objectives a research program has been developed that consists of (i) Laboratory studies, focusing on specific mechanistic aspects of chemical dynamics, (ii) Field studies, testing and validating laboratory findings under field conditions, (iii) Computer modelling, which enables calculations involving the complexities encountered in the field, and which provides an up-to-date knowledge-base in an accessible and applicable form. To illustrate our research strategy, we present a summary of our studies of the chemical exposure dynamics in forage fish. The main objective of this presentation is to demonstrate how laboratory studies, field studies and food-chain/ecosystem modelling can be integrated to interpret biomonitoring data in terms of ambient contaminant levels in water and sediments of aquatic systems and in terms of chemical loads into the system.

B16

PCB DYNAMICS OF
POTTERSBURG CREEK, LONDON ONTARIO

Danuta Zaranko

K. Solomon and N. Kaushik
Department of Environmental Biology
University of Guelph
Guelph, Ontario. N1G 2W1

INTRODUCTION

In recent years, the mechanism for contamination in biota, especially top predators, has been greatly debated. Early food chain modelling embraced the concept of bioconcentration as being the mechanism responsible for the observed body burdens in aquatic organisms (Schneider 1982; Duursma et al. 1989). Bioconcentration states that the concentration in an aquatic organism can be attributed to the chemical concentration in the water, the octanol/water partition coefficient, and the lipid fraction of the organism. Considerable evidence has shown that this relationship does not always hold true for many organic chemicals including PCB's. Many experiments have shown that aquatic organisms are capable of bioaccumulating PCB's above concentrations which would be expected from water alone (Oliver and Niimi 1985; Gobas et al. 1987.). This would suggest that some other mechanism, such as biomagnification (ie. the uptake of a chemical through ingestion), is responsible for the contaminant levels in aquatic biota, especially those occupying the top of food chains (Thomann 1987; Shaw & Connel 1986).

The discovery of PCB contamination in Pottersburg Creek, London, Ontario, has provided an opportunity in gaining a better understanding of the movement of PCBs in aquatic ecosystems and the mechanism of PCB transfer to higher trophic levels. Moreover, the ultimate objective of this project is to develop a model in order to predict the time required for PCB levels in aquatic biota to reach the IJC (1975) aquatic life protection guideline of 100 ng/g.

MATERIALS AND METHODS

Collection and analyses of stream components, 1988 - 1989.
Samples of algae, aquatic macrophytes, various macroinvertebrates and fish were collected for biomass and PCB analysis at 4 sites along Pottersburg Creek (Fig.1). Water and sediment samples were collected by the Ministry of the Environment. Station 1 was the control site and Stations 2, 3 and 4 were located downstream of the point of contamination.

Invertebrates gathered for biomass and density determination were collected with a T-sampler enclosing an area of $0.052 m^2$, and sieved through a 300 μm bag. The samples were picked live in white enamel trays and subsequently preserved in 70% ethanol for later identification and enumeration. All organisms were identified to the lowest taxonomic level practical, usually genus,

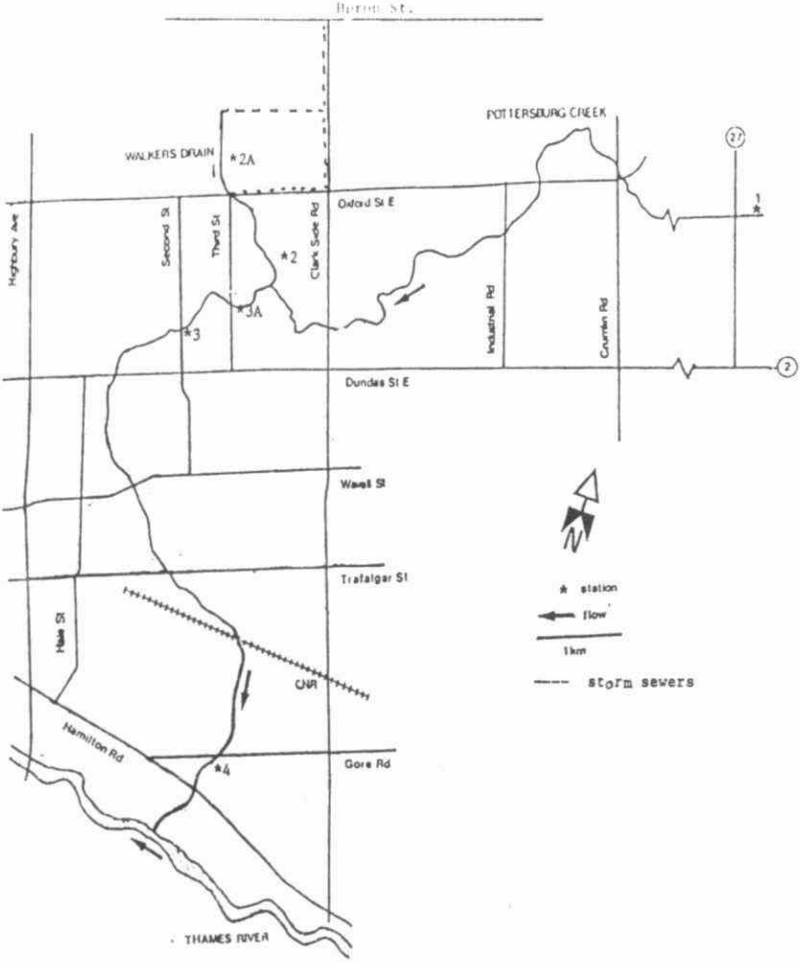

Figure 1: Location of monitoring stations along Pottersburg Creek, Walker Drain and the Thames River, in London, Ontario.

except for oligochaetes which were identified to species.

Invertebrates gathered for PCB analysis were collected with sieve buckets and picked live in white enamel trays until an adequate weight was obtained for analysis (ie. 3g or more). Animals were separated into their respective classes (eg. oligochaetes, chironomids, leeches) and weighed to the nearest 0.01g. Samples were subsequently wrapped in hexane-rinsed aluminum foil, placed in plastic Whirl-Pak bags and kept frozen until analysis. The samples were analyzed for total PCBs and results were reported on a wet-weight basis. Analyses were carried out at the Ontario Ministry of the Environment's laboratory in Rexdale using packed column gas chromatography.

Construction of a Food Web

Fish were collected with a seine net from Stations 1,2,3 and 4 and preserved in formalin. Collections were made in the summer and winter of 1988 and the summer of 1989. Fish stomachs were dissected and a list of food items was compiled. A food web of Pottersburg Creek was synthesized from feeding observations and gut contents analysis. Points of PCB entry and loses were also identified.

Determination of PCB uptake and depuration rates

Uptake experiments were set up for the following biota: crayfish, leeches, fish, and oligochaetes. Crayfish were captured in the fall of 1989 from the Eramosa River, Guelph, Ontario. A total of 32 crayfish were placed in wire cages measuring 15cm x 15cm x 15cm, with 4 crayfish per cage. Leeches (*Nephelopsis obscura*) were purchased from a local bait dealer. Approximately 15 leeches were placed in each of 5 triangular cages (30cm sides) made of wire and nylon screen which had a mesh size of 2mm. Creek chub (*Semotilus atratulus*) were collected from the control site, Station 1. Approximately 35 fish were placed in a single wire cage 80cm x 80cm x 15cm. Oligochaetes were purchased from a local pet store and approximately 15 grams of worms were placed in each of 5 metal tins (15cm height, 10 cm diameter) containing PCB contaminated sediments collected from Station 2. The sediments were sieved through a 300um screen to remove indigenous worms and large particulate matter. The tops and bottoms of each can were replaced with 300um mesh screening and secured with rubber bands.

The cages containing the biota were anchored to the stream bed with bricks at the contaminated site (Station 2) and subsequently collected after 4,6,10,18 and 34 days. Control groups were placed at the uncontaminated site, Station 1, and collected after 34 days. Each group of animals was weighed live to the nearest 0.01g, wrapped in hexane-rinsed aluminum foil, placed in Whirl-Pak plastic bags, and frozen until analysis. Three replicate samples were submitted for each time period. In addition, samples of all groups of animals were submitted for pre-exposure analysis .

The experimental design and protocol was the same for the depuration study with the exception that the animals were collected from the contaminated site (Station 2), and anchored to the stream bottom at the control site (Station 1).

RESULTS AND DISCUSSION

PCB residues in algae and aquatic macrophytes

In 1988, algae (*Cladophora sp.*) and aquatic macrophytes (*Potamageton sp.*) collected at Station 2 were able to accumulate substantial quantities of PCBs, 150 ng/g and 770 ng/g, respectively. No PCBs were detected in algae and aquatic macrophytes at Station 3. Several authors have documented the uptake of chlorinated hydrocarbons by phytoplankton (Biggs et al. 1980; Sodergren and Gelin 1983) aquatic macrophytes (Strek and Weber 1982) and filamentous algae e.g. *Cladophora sp.*, (Mowrer et al. 1982; Larsson 1987). Phytoplankton and Cladophora are able to rapidly sorb PCBs from the water and the uptake initially follows first order kinetics (Larsson 1987). Thus, the partitioning process governs PCB uptake and in turn is dependent on the concentrations of PCBs in the water (Larsson 1987). In March 1988, PCB concentrations in water at Station 4 were 680 ng/g. PCBs bound to sediments may be redistributed to the water by bioturbation (the activity of benthic invertebrates in the sediment), and desorption (Klump et al. 1987; Karickhoff and Morris 1985) and thus made available to algae and phytoplankton.

As no metabolism or elimination of PCBs has been recorded in algae (Hutzinger et al. 1974), the rapid adsorption and uptake of PCBs by algae and aquatic macrophytes constitute an additional means for the introduction of these compounds into food webs (Mahanty 1986). Algae and aquatic macrophytes are consumed by scrapers, ie. snails and shredders,ie. crayfish. Algae are also consumed by a variety of fish in Pottersburg Creek. Analysis of gut contents has revealed that filamentous algae are the primary diet of the northern redbelly dace (*Chrosomus eos*) and the stoneroller (*Campostoma anomalum*). Common shiners (*Notropis cornutus*) and blacknose dace (*Rhinichthys atratulus*) also consume filamentous algae but to a lesser extent. Thus algae and aquatic macrophytes appear to be significant vectors in the transfer of PCBs to the higher trophic levels in Pottersburg Creek.

PCB residues in snails and crayfish

PCB residues in snails and crayfish can be attributed to the consumption of algae and aquatic macrophytes. In 1988, *Helisoma sp.* collected from Station 3 had a PCB residue of 360 ng/g and young of the year crayfish from Stations 2, 3 and 4 had residues of 960 ng/g, 720 ng/g and 320 ng/g, respectively. No PCBs were detected in Station 1 biota. Decreasing body burdens in crayfish indicate a reduction of PCB availability with increasing distance from Walkers Drain (Stn. 2). Older crayfish from Station 3 were noted to accumulate 40% more PCBs than young of the year. This would suggest that length of exposure, coupled with higher lipid levels in the older individuals, may have an effect on PCB bioaccumulation. In addition, crayfish eat detritus, and other organisms

(Hynes 1970), which in turn are known to accumulate or sorb PCBs. Thus, bioaccumulation may be further facilitated via this pathway and account for the higher body burdens observed in crayfish.

In 1989, snails collected at Station 3 showed no accumulation of PCBs, however, these may have recently drifted from upstream uncontaminated areas. Consequently residues may not reflect true availability. PCB residues in crayfish collected from Station 2, 3 and 4 varied depending on the size of the animal as well as the lipid content albeit, concentrations were noted to be lower than in the previous year. Crayfish and snails are eaten by a variety of fish (Scott & Crossman 1972). Gut contents analysis confirmed the ingestion of snails by creek chub (*Semotilus atromaculatus*) in Pottersburg Creek, however no crayfish were found in the stomachs of the fish. Therefore, snails serve as a vector for the distribution of PCBs to fish which occupy a higher trophic level.

PCB residues in oligochaetes and chironomids

PCB residues in oligochaetes and chironomids were among the highest for 1988 biota, reaching concentrations of 3030 ng/g and 1890 ng/g respectively in the summer months. Initial bioaccumulation by midges has been shown to be very rapid with steady state concentrations being reached in 4 to 5 days (Swindoll & Applehans 1987). In addition, benthic organisms, such as worms and chironomids, ingest sediment (Roberts and Meier 1982) and PCB contaminated organic particles after they settle on the sediment (Landrum & Scavia 1983; Oliver 1984). Meier and Rediske (1984) have been able to show that larvae of the midge *Glypotendipes barbipes* can accumulate significant concentrations of PCBs from substrate feeding alone. Ingestion increases exposure surfaces as well as decreases distances for diffusion and thus facilitates uptake of sediment-sorbed compounds (Swindoll & Applehans 1987).

In 1989, PCB concentrations in worms and chironomids have decreased to 900ng/g and 200ng/g respectively perhaps reflecting a decrease in the availability of these lipophilic compounds to lower trophic level organisms.

PCBs have been shown to be poorly eliminated from benthic organisms (Swindoll & Applehans 1987; Meier & Rediske 1984). In Pottersburg Creek analysis of fish stomachs has shown that midge are consumed by almost all fish. In addition, several authors have shown that fish such as creek chub consume worms (Gilliam et al. 1989). Thus it is probable that chironomids and worms serve as major vectors for the contamination of the higher trophic levels ie. fish and leeches.

PCB residues in leeches

In the summer of 1988, PCB residues in leeches were 2000 ng/g at Station 2 and 1060 ng/g at Station 3. In 1989, residues dropped to 1100 ng/g at Station 2 and 700 ng/g at Station 3. The observed PCB concentrations in leeches can be attributed to the close proximity of the animals to the sediments but the main route is through ingestion of contaminated prey. Leeches (*Erpobdella punctata punctata*) captured from Pottersburg Creek were observed eating chironomids in captivity. As well, several authors have documented that the main food items of leeches are oligochaetes and chironomids (Davies et al 1981; Anholt 1986). The decrease of PCBs in leeches mirrors the decrease in their prey whereas sediment concentrations have fluctuated over the two year period.

Leeches are preyed upon by a variety of fish (Scott & Crossman 1973) but were only found in one fish from Pottersburg Creek. Therefore, it was concluded that leeches serve as intermediate vectors of PCBs transfer to fish in the creek.

PCB residues in fish

Eleven species of fish have been identified from Pottersburg Creek and can be grouped into four categories based on their primary diet: algae grazers; chironomid feeders; bottom ooze feeders; and general feeders.

Common shiners (*Notropis cornutus*) collected in July 1988 had lower PCB residues than johnny darters (*Etheostoma nigrum*) collected from the same stations. The observed differences can be attributed to the position of the fish in the water column as well as their diet. Johnny darters were found to feed primarily on chironomids which themselves exhibited very high PCB levels. On the other hand, analysis of common shiner fish stomachs revealed no preferred diet. However, it was noted that in the spring and early summer, their diet consisted primarily of surface insects. Gilbert (1964) found that common shiners usually feed off the surface but will take food off the bottom. In the fall and winter months, the common shiner switches its diet to detritus, sediment, silt or invertebrates depending on their respective availabilities. Thus, depending on the time of year, PCB residues in common shiners may vary depending on their diet.

PCB concentrations in common shiners and johnny darters varied in 1989 depending on station location and lipid content. Moreover, it was noted that PCB concentrations in both species of fish did not decrease over the two year period perhaps as a result of biomagnification as fish occupy the highest trophic level.

Food web of Pottersburg Creek

A synthesized food web of Pottersburg Creek is presented in Figure 2. Chironomids and worms are the major food items of almost all fish species except the northern redbelly dace and the stoneroller whose primary diet is filamentous algae.

Uptake and depuration rates

Preliminary uptake and depuration experiments (Table 1) have shown that invertebrates and fish are able to accumulate PCBs in a short period of time. Worms accumulated 400 ng/g PCB in 24 days while leeches accumulated a maximum of 160 ng/g in 18 days which then dropped to 120 ng/g after

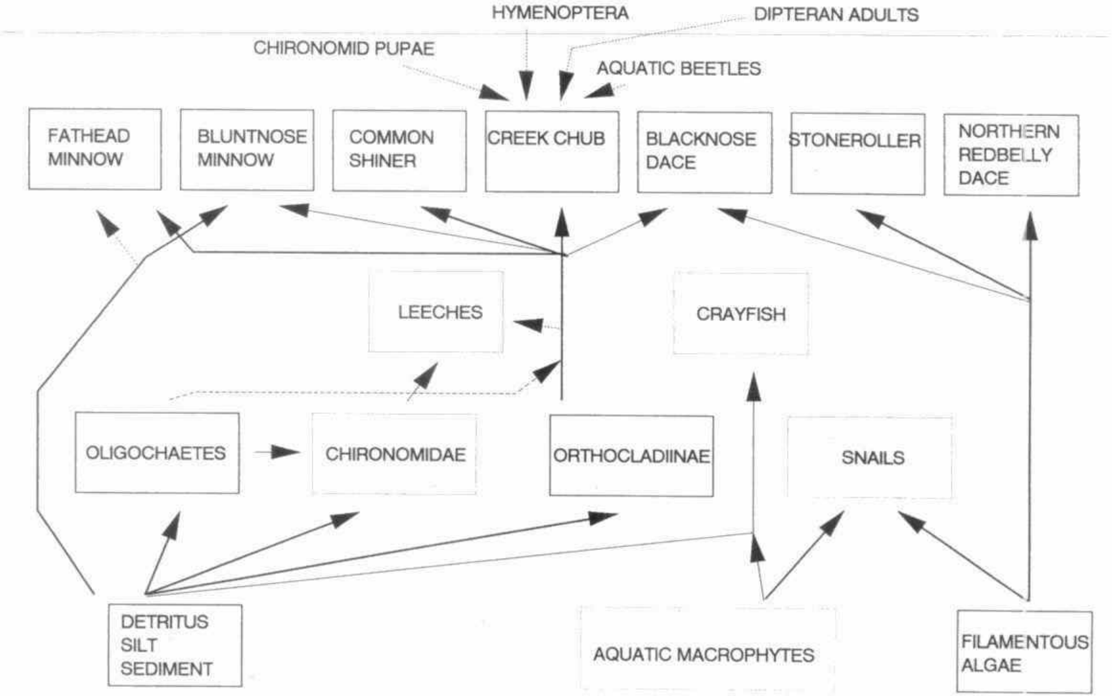

FIGURE 2: FOOD WEB OF POTTERSBURG CREEK, STATION 2 ,SPRING-SUMMER.

28 days. However accumulations are not of the same magnitude as those of the resident biota collected in 1988 and 1989. Lower accumulations may be attributed to the short maximum time interval ie. 34 days, therefore, subsequent uptake and depuration experiments will be conducted for a longer period of time. In addition, the control experiments, which ran parallel to the uptake and depuration experiments, revealed that the cages were exerting a significant amount of stress on the animals resulting in weight loss and mortality. This was particularly evident in fish and crayfish who only accumulated approximately 40 ng/g PCB and 100 ng/g in 34 days. For these reasons, initial cages will be modified to minimize stress and allow foraging.

Modelling

Upon the completion of the uptake and depuration experiments, all available information and data collected from Pottersburg Creek will be integrated and placed into an ecological framework. PCB transfer rates between the different components of the stream (ie. fish, invertebrates, water, plants, etc.) will be deduced mathematically and subsequently incorporated into a simulation model in order to explore PCB dynamics in stream ecosystems. However, as all results are not yet available, modelling is still to be completed.

CONCLUSION

As reflected in the data, PCB concentrations in biota, water and sediments from Pottersburg Creek appear to be decreasing with time as well as along the length of the creek away from the point source. However, PCB residues in aquatic biota still remain above the IJC aquatic protection guideline of 100 ng/g indicating that a continuing source of PCBs remains within the creek or is entering the creek periodically.

From within the creek, the sediments are implicated as being a continuing source of PCBs to the biota. Scouring of bottom sediments caused by catastrophic drift, bioturbation and desorption processes continuously redistribute PCBs making them more available to aquatic biota. In addition, water and sediment samples collected from the storm sewer networks indicate that during times of heavy rainfall, there is a substantial influx of PCBs into the creek. The coupling of all these processes has attributed to the observed high PCB accumulations in biota. It is suggested that further biomonitoring of Pottersburg Creek continue until PCB levels in biota drop below 100 ng/g.

ACKNOWLEDGEMENTS

The authors are thankful to the Ontario Ministry of the Evnironment for financial assistance.

TABLE 1: PCB concentrations in caged biota from Pottersburg Creek, London, Ontario. Uptake and depuration experiments, 1989.

BIOTA	DATE	LOCATION OF CAGES[stn.]	DAY	SAMPLE WEIGHT (g)	% LIPIDS	PCB'S (ng/g)
CRAYFISH	89/10/03	-	Day 0	8.3	0.9	<20
[Orconectes propinquus]			uptake	7.24	2.6	<20
uptake				8.18	0.9	<20
	89/10/07	2	Day 4	4.57	2.9	70
				5.03	4.0	<20
				7.19	2.0	<20
	89/10/09	2	Day 6	7.35	1.9	<20
				8.85	1.5	<20
				6.77	?	?
	89/10/13	2	Day 10	6.62	2.6	<20
				6.88	2.2	<20
				5.26	2.4	<20
	89/10/21	2	Day 18	12.47	1.8	<20
				6.90	1.7	<20
				4.40	2.6	80
	89/11/06	2	Day 34	7.30	2.6	150
				7.87	1.7	70
				8.84	2.9	100
	89/11/06	1	Day 34	3.72	3.3	<20
			control	7.32	2.6	<20
LEECHES	89/09/27	-	Day 0	4.48	2.3	<20
[Nephelopsis obscura]			uptake	3.72	2.9	<20
uptake				3.11	3.1	<20
	89/09/27	2	Day 4	10.41	3.0	<20
				6.16	2.6	<20
				7.9	3.1	<20
	89/09/29	2	Day 6	8.73	2.7	40
				10.97	2.9	40
				8.08	2.0	50
	89/10/03	2	Day 10	3.63	3.6	60
				3.20	3.9	100
				3.81	3.6	100
	89/11/02	2	Day 18	4.88	2.2	160
	89/11/12	2	Day 28	3.06	2.7	120
	89/11/02	1	Day 40	3.71	3.9	<20
			control	4.15	4.6	<20
FISH	89/10/09	-	Day 0	26.60	1.6	<20
[Semotilus atratulus]				17.92	1.6	<20
Uptake				14.27	1.5	<20
	89/10/13	2	Day 4	21.86	2.0	<20
				16.61	1.8	<20
				16.68	2.0	<20
	89/10/15	2	Day 6	18.01	1.8	<20
				21.07	2.0	<20
				12.95	1.5	30

TABLE 1: [Cont..]

BIOTA	DATE	LOCATION OF CAGES[stn.]	DAY	SAMPLE WEIGHT (g)	% LIPIDS	PCB'S (ng/g)
	89/10/19	2	Day 10	21.42	1.8	30
				19.44	1.6	<20
				10.86	2.4	40
	89/10/27	2	Day 18	14.29	1.5	40
				17.27	1.5	<20
				23.19	1.6	<20
	89/11/12	2	Day 34	11.66	1.9	60
				10.33	2.3	40
				8.09	1.4	60
WORMS uptake	89/10/09	-	Day 0	5.18	7.7	<20
				5.00	7.8	<20
	89/10/13	2	Day 4	3.02	5.2	230
				3.02	5.9	200
	89/10/15	2	Day 6	3.92	4.3	230
	89/10/19		Day 10	5.44	5.7	380
	89/10/27	2	Day 18	2.25	4.3	270
	89/11/02	2	Day 24	2.19	5.4	400
FISH [Semotilus atratulus] depuration	89/10/03	-	Day 0	26.62	2.5	650
				18.67	1.5	650
				18.81	1.8	230
	89/10/07	1	Day 4	26.57	13.9	1000
				22.21	3.0	720
				20.98	1.2	400
	89/10/09	1	Day 6	12.30	0.3	2000
				24.23	1.3	475
				14.97	5.0	600
	89/10/13	1	Day 10	14.17	1.4	450
				14.90	0.8	900
				7.74	3.2	730
	89/10/15	1	Day 0	16.83	2.2	680
			2nd set	14.07	1.3	1850
	89/11/02	1	Day 18	21.88	1.7	720
				12.05	10.3	700

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VOLUME I

SESSION B

WATER QUALITY RESEARCH

POSTER PRESENTATIONS

DEVELOPMENT OF AN IMPROVED SYSTEM FOR THE APPLICATION OF POWDERED ACTIVATED CARBON IN POTABLE WATER TREATMENT

by

Heather Donison, Andrew Benedek
ZENON Environmental Inc., Burlington, Ont.

Powdered activated carbon (PAC), is widely used in Ontario and around the world for the removal of taste and odour from drinking water. More recently PAC has been finding use in the removal of toxic organics from drinking water either in the case of chronic low level contamination or occasional high levels resulting from an accidental spill. ZENON Environmental Inc. has undertaken a study for the Ontario Ministry of the Environment to develop an improved system for the application of PAC in water treatment plants and to develop a concept for a portable system suitable for response to specific short term treatment needs.

The Phase 1 study included the following:

1) Literature review
2) Identification of PAC systems
3) Development of process design criteria
4) Selection of two most promising PAC systems
5) Bench scale development and evaluation of two systems
6) Selection of one system for demonstration

Conventional PAC drinking water treatment for taste and odour control is by slurry addition prior to coagulation/sedimentation or granular filtration. The literature search did not reveal any alternative PAC contacting or separating systems being used or developed for drinking water treatment, however, a wide variety of systems for wastewater treatment are being used or developed. Two conventional PAC contacting and separation systems and ten alternative PAC systems were identified as potentially applicable for toxic contaminant removal from drinking water and suitable for initial evaluation.

The following criteria were established and used to evaluate the potential reactor alternatives.

a) Contact time greater than one minute.
b) Contact stratification.
c) Reliable separation.
d) Spill response.
e) Adaptable to existing facilities.
f) Process reliability.
g) Mechanical reliability.

Downflow PAC packed bed filtration and multistage crossflow filtration met all of the criteria and were selected for development at bench scale.

In bench scale testing performance of downflow PAC packed bed filtration was proven to be unreliable due to the development of channels through the bed.

Crossflow ultrafiltration (UF) was proven to effectively separate PAC from an aqueous stream. The UF fluxes observed were relatively high and stable. A multistage UF system is necessary to achieve contact stratification but is technically feasible for the removal of toxic organics from drinking water.

In the second phase of work a pilot scale Powdered Activated Carbon/Cross Flow Filtration PAC/CFF system was constructed and operated at the Brantford Water Treatment plant.

The performance of the system was evaluated at different operating conditions and with odour and other organic chemicals spiked into the feed. The CFF flux was consistent and stable during the tests averaging 114 L/m^2/hr. The process consistently removed turbidity to less than 0.03 NTU and total coliforms to less than 2 counts/100 ml. The removal of dissolved organic carbon (DOC) and total trihalomethane forming precursors (TTHMFP) was marginal at PAC dosages of 5-10 mg/L but significant (25% and 35% removal) at higher dosages of 56 mg/L.

The capital and operating costs for 1 MGD and 0.1 MGD PAC/CFF systems were estimated. The total costs for the 1 MGD PAC/CFF treatment ($2.38/1,000 gal) are higher than for conventional coagulation/filtration treatment followed by GAC ($1.52/1,000 gal). The total cost for the 0.1 MGD PAC/CFF treatment process at a high PAC dosage of 1,000 mg/L is $6.22/1,000 gal.

The treatment costs for the PAC/CFF are high but the process has the following advantages:

1) Provide guaranteed removal of turbidity and bacteria.
2) Easy startup and suitable for operation with minimal attendance.
3) Requires no guesswork or chemicals to obtained required treatment.

In view of these advantages the system is a viable response to emergency situations but may not be suitable as a replacement for conventional treatment followed by GAC unless the feed water is highly variable in turbidity or colour. With time, as membrane costs become lower however, the cost as well as water quality advantage are likely to favour this option for permanent systems.

Geochemical Associations of Cd, Cu, Pb and Zn with Suspended Particulates in the Don River. Lesley A. Warren* and Ann P. Zimmerman. Department of Zoology, University of Toronto, Toronto, Ontario, Canada.

The Don River drains a highly urbanized watershed of 376 km^2 and runs approximately 30 km through Metropolitan Toronto before discharging into Lake Ontario through the Keating Channel. There are over 1400 street run-off and industrial discharge outfalls on the river as well as a major sewage treatment plant and a snowmelt yard. Increasing problems with contaminated sediments in the Keating Channel and the Harbour have led to questions about sources of sediments and associated metal loads, development of in-place pollutants, relationships between sediment composition and water quality and whether in-place pollution and its effects on aquatic ecosystems can be predicted.

The purpose of the present study was to investigate the geochemical associations of 4 trace metals, Cd, Cu, Pb and Zn, within the pool of total SPM *in situ* in the Don River, located in Metropolitan Toronto; and to determine the relative importance of various trace metal pools in the SPM fraction as trace metal carriers within this system. This work represents the first phase of a larger ongoing study on the Don to determine the role of SPM as a transport vector of trace metals, and whether predictive relationships among specific discharge sources of metals and/or solids to the Don, and the geochemical associations of trace metals with SPM *in situ* can be derived.

A total of 37 suspended sediment samples were collected at 4 sites on the Don River over a 12 month period. These samples were analyzed for the trace metals Cd, Cu, Zn and Pb in 4 operationally defined geochemical phases:(1) Leachable ("exchangeable and carbonate associated"); (2) Reducible ("oxides"); (3) Oxidizable ("organics"); and (4) Residual ("mineral phases"). While concentrations of suspended sediment and total metal were highly variable in time and space, in general there was an increase in both in a downstream direction, thus, increasing metal loads in this direction. Metal speciation patterns were relatively constant despite variability in absolute concentrations. With the exception of Cd, very small proportions of metal were found associated with the exchangeable fraction. Cu was the only metal found in high proportions associated with the organics fraction. The two major sediment carrier phases in the Don River are the oxides and residual minerals. As these phases form stable complexes with trace metals, the fate of trace metals in this system is intimately tied to the suspended particulate fraction. PCA analyses showed that a major proportion of the variance in metal concentrations is explained by geochemical phase.

THE EFFECTS OF AGRICULTURAL DRAINAGE ON SEDIMENT AND WATER QUALITY LOADINGS.

J.D. Paine*, W.E. Watt, S.A. Peters, Department of Civil Engineering, Queen's University, Kingston, Ontario K7L 3N6.

INTRODUCTION

The principal objective of this project was to gain an understanding of the pathways and fates of agricultural chemicals (fertilizers and pesticides) applied to tile-drained fields. Removal of valuable pesticides, fertilizers and topsoil by surface or subsurface drainage represents an economic loss to agriculture and a potential pollution hazard to receiving waters. In order to evaluate this potential impairment of water quality, there is a need for accurate prediction of chemical contaminant and sediment loadings for different environments, loading conditions, and agricultural management strategies. This then is an area of interest to both the agricultural community and Environment Ontario. The specific objectives of the work were (i) to develop a continuous, physically-based hydrologic simulation model to represent processes for contaminant transport on the surface, through the soil profile and into the tile drains; (ii) to undertake field studies to define the model's physically-based parameters such as saturated hydraulic conductivity, soil type and depth, drainable porosity, infiltration characteristics, chemical transport and decay coefficients; (iii) to test agricultural management practices in conjunction with prevailing climate as they may influence nutrient or pesticide loss from the fields through the tile drains.

MODELLING TRANSPORT AND FATE OF PESTICIDES UNDER TILE DRAINAGE

A previous research project funded by Ontario Environment involved the development of TILE, a continuous, physically-based hydrologic (water quantity) simulation model for tile-drained agricultural fields and basins. The challenge in development of water quality algorithms for use with the existing model was to incorporate significant processes within the existing framework in order to model chemical constituent storage, transport and transformation.

The conceptual representation of constituent migration within the framework provided by the TILE hydrologic model is illustrated in Figures 1 and 2. The control volume modelled is a single tile-drained agricultural field. Water is input as rainfall and exits by way of evapotranspiration, tile flow or surface runoff.

Constituent mass is input by human application and is allowed to leave through tile flow, surface runoff and a loss function which replicates the effects of a number of chemical and physical loss processes.

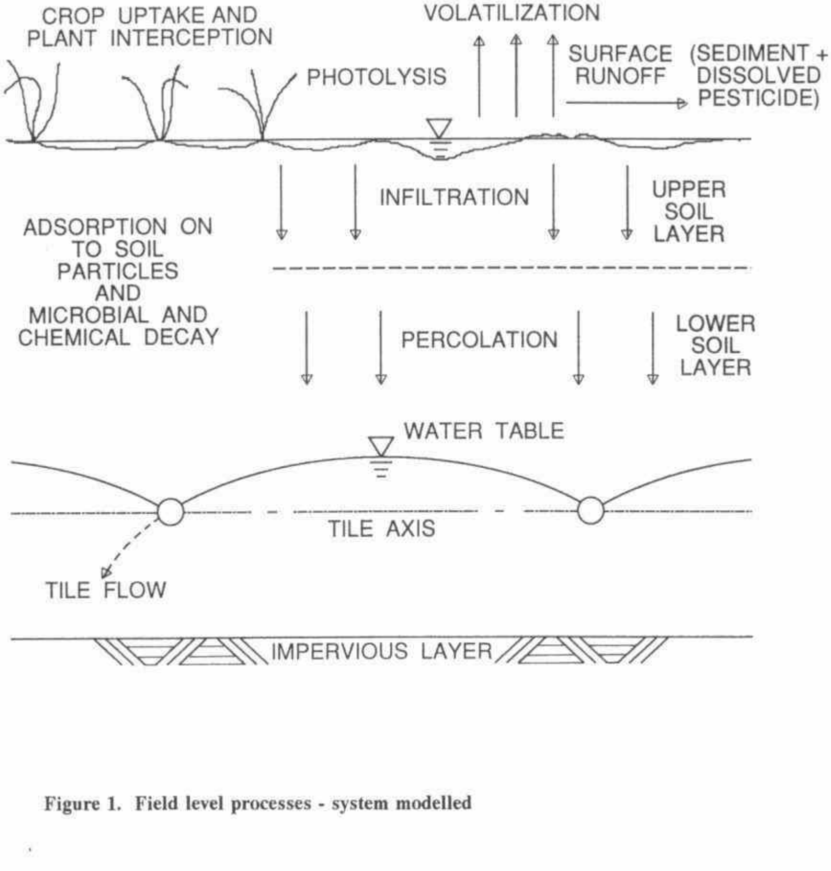

Figure 1. Field level processes - system modelled

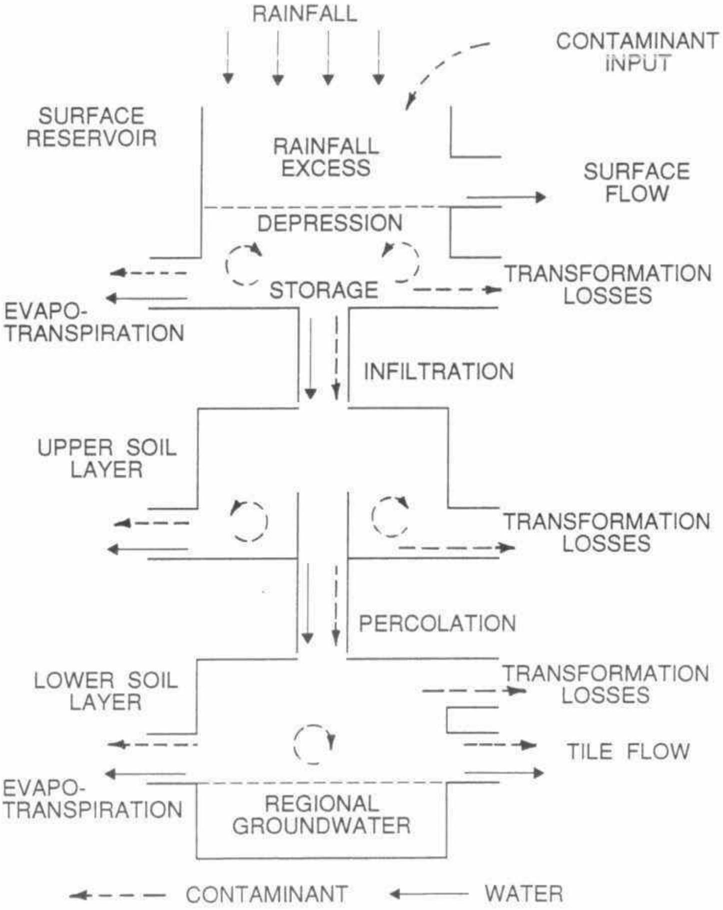

Figure 2. Conceptual representation - water quality model

Constituent mass storage is modelled by three storage reservoirs:

i) a surface storage reservoir which allows for the constituent to leave the system through the control volume boundary carried by generated surface runoff or to enter the soil storage reservoirs along with infiltration water,

ii) an upper soil layer storage reservoir from which the constituent mass may enter the lower soil storage reservoir through percolation, and

iii) a lower soil layer storage reservoir from which the constituent mass may be discharged and lost to the system through tile drainage.

Constituent mass transmission pathways are:

i) application of the constituent mass to the field by human action,

ii) routing of constituent mass to the edge of the field by surface flow and subsequent loss of the mass through the control volume boundary,

iii) migration of constituent mass from the surface mass storage reservoir to the upper soil layer along with infiltration water,

iv) migration of constituent mass from the upper soil layer storage reservoir to the lower layer along with percolation water, and

v) routing of constituent mass to the tile drains and subsequent loss to the control volume through tile flow.

The TILE quality model allows for application of a loss function conceptualized to represent a number of physical, chemical and biological processes acting within the agricultural field system to reduce the constituent mass available for transport to all three of the mass storage reservoirs. The most significant processes lumped within the representative loss function are dispersive or turbulent flow distortions to advective constituent transport, constituent adsorption onto soil particles, and physical (photolysis, volatilization), chemical (hydrolysis and other chemical reactions) and biological (microbial decay and plant interception) transformation processes.

Methodologies by which agricultural chemicals are applied to farm fields can be divided into two categories: i) surface application by which the chemical is placed onto the soil surface as a liquid spray or solid broadcast, and ii) subsurface application where the chemical is incorporated directly into the upper layer of the soil. Subsurface application is becoming more popular since it is believed to reduce post-application losses due to wind action, surface runoff and transformation processes such as volatilization and photolysis. The model allows for specification of the application method by the user in conjunction with specification of the time of application. If a surface application method is indicated, the program responds by assigning the input mass to the surface storage reservoir. If, however, an incorporation method is specified, the input mass is assigned directly to the upper soil storage reservoir.

Pesticides commonly applied to farm fields are often formulated as powders or liquids with low solubilities in water. To provide an accurate model of the behaviour of such undissolved chemical species, two procedures were incorporated into the TILE quality model. The first procedure allows the user to input a laboratory or field-corrected solubility in water for the chemical constituent of interest. The model responds to the input solubility value by limiting the amount of chemical permitted to dissolve in the water available in a specific reservoir to the level provided for by the chemical solubility. In addition to the chemical solubility in water, review of the physical system of an agricultural field indicates that there will be a limiting quantity of water below which it is unlikely that a chemical could be dissolved and mixed uniformly within a particular storage reservoir. The TILE quality model allows for consideration of this 'mobility threshold' for each of the chemical application methodologies. If surface application is specified, then the mobility threshold corresponds to a minimum depth of water present in depression storage as a result of water inputs to the system. Thus it is possible for a small amount of rain to fall upon the field and infiltrate into the upper soil storage reservoir without causing any chemical mass to move with it. If, however, an incorporation method is chosen, then the mobility threshold necessitates that the specified volume of water above the field capacity be present within the upper layer soil storage reservoir for solution, mixing and transfer of the chemical constituent to occur.

MODEL TEST RESULTS

The use of the model for both real and synthetic rainfall events demonstrated the relative importance of i) pesticide application methods, ii) rainfall occurrences following application, and iii) soil characteristics on the transport of contaminants to the tile drains and thence to receiving waters. The poster display illustrates water quantity and quality hydrographs for differing situations noted above. Of particular interest is the half life of the pesticide in the upper layer (where it is available for crop uptake) for the various rainfall sequences and application methods modelled.

BP4

CHRONIC EFFECTS OF THIOCYANATE ON FRESHWATER FISH: DEVELOPMENT OF A WATER QUALITY CRITERION

R.P. Lanno and D.G. Dixon*

Department of Biology, University of Waterloo
Waterloo, Ontario, N2L 3G1
(518) 885-1211

Thiocyanate (SCN$^-$) is an inorganic anion that has specific antithyroidal properties as an inhibitor of iodide (I$^-$) uptake and organification (Wolff, 1964; Yamada et al., 1974; Green, 1986). The antithyroidal properties of SCN$^-$ have been recognized in mammals for some time, but investigations regarding antithyroidal effects in aquatic organisms have been limited to endocrinological studies in which SCN$^-$ was administered by intraperitoneal (ip) injection (Singh, 1969; Singh et al., 1977; Eales and Shostak, 1983).

Thiocyanate has also been found to inhibit halide transport across biological membranes such as gills (De Renzis, 1975; Epstein et al., 1975; Maetz, 1976), and possibly the intestine (Katz et al., 1982), as well as reduce phosphorous (P) and I$^-$ uptake by ovaries (Lindsay et al., 1966; Singh et al., 1977).

Cyanide (CN$^-$) is used by the mining industry in the extraction and concentration of gold from gold ores. As a result, cyanides are routinely present in mine effluents in considerable quantities. This situation has long been recognized as an environmental problem and has resulted in the establishment of an Ontario water quality objective for CN$^-$ (0.005 mg/L, as HCN) (Ontario Ministry of the Environment, 1984).

The detoxification and recovery of CN$^-$ from gold mill effluents often results in the presence of significant amounts of SCN$^-$ in mill effluents. Thiocyanate levels of up to 168-680 mg/L have been detected in effluents following SO_2-air treatment (Huaitt et al., 1983). Metabolic SCN$^-$ may be formed by aquatic organisms during the detoxification of CN$^-$ present in industrial effluents or from the metabolism of naturally occurring dietary CN$^-$ precursors, such as cyanogenic glycosides and nitriles.

Based upon lethality data (Doudoroff, 1976; Heming et al., 1985; Speyer and Raymond, 1988), SCN$^-$ appears to be much less toxic than CN$^-$. Information on the chronic toxicity of SCN$^-$ in fish is absent, although implications have been made (Leduc,

1984) that the chronic effects of CN^- exposure may actually be due to SCN^-. Due to the lack of sufficient information on the chronic toxicity of SCN^-, there is currently no water quality objective for SCN^- in Ontario.

The objective of our research was to obtain sufficient data on the chronic toxicity of SCN^- on survival, growth, metabolism, and reproduction of freshwater fish to permit the development of a water quality criterion.

The study has been divided into four phases:

1) A 16 week exposure of rainbow trout fry to SCN^- to determine effects on survival, growth, and physiology,

2) A life-cycle study to determine the impact of sublethal SCN^- exposure on the reproductive capacity of fathead minnows,

3) A 16 week exposure of rainbow trout fry to SCN^- or CN^- to determine the contribution of CN^- to sublethal SCN^- toxicity, and

4) A preliminary field study to determine if SCN^- is present in waters receiving effluent from gold mines and if physiological changes detected in laboratory fish in response to sublethal SCN^- exposure were present in feral fish.

METHODS AND RESULTS

Chronic rainbow trout exposure studies

Triplicate groups of juvenile rainbow trout (3 g) were continuously exposed to nominal SCN^- concentrations of 40, 80, 120 and 160 mg/L for 16 weeks. Trout were pair-fed a practical trout diet (GRT-70) (Cho et al., 1974) and weighed every two weeks to determine growth rates and provide a routine stressor to measure the expression of Sudden Death Syndrome (SDS) within each treatment population. Feed intake and mortalities were monitored daily.

At the end of the 16 week growth study, fish were anaesthetized in MS222, killed by cervical dislocation, and length, weight, splenosomatic and hepatosomatic indices, hematocrit, and hemoglobin were measured. Plasma samples for the colourimetric determination of total cyanide-reactive substances (Lambert et al., 1975) and thyroxine (T_4) were obtained by caudal peduncle severance. For thyroid histology, the entire lower jaw was removed from treated and pair-fed control fish, fixed in 10% buffered formalin, sectioned longitudinally, and stained with hematoxylin and eosin for routine histological observation.

Data were examined for normality and homogeneity of variance by the examination of residuals. One-way ANOVA, using $\log_{10}$ transformed data, was used to determine separately the effects of treatment levels and control food consumption levels on the response variables. Two-way ANOVA was then used to detect differences between treatments and their matched controls.

Mortalities and physical observations

Mortalities increased with SCN^- concentration, with all fish exposed to 160 mg/L dying by 12 weeks, and approximately 40% of the fish exposed to 120 mg/L dying by the end of the growth trial. SDS was apparent at the two highest concentrations of SCN^-, with varying proportions of the population at each treatment expressing SDS after weighing. Mortalities in the 40 and 80 mg SCN^-/L groups were minimal.

Cranial deformities were expressed to a varying degree in all SCN^--exposed trout, the severity of deformity increasing with SCN^- concentration. This condition was characterized by the small size of the head of the trout in relation to the body. Operculae were often shortened or crumpled, exposing gill filaments. Pigmentation changes were apparent as the transitory darkening of individual fish within tanks receiving thiocyanate.

Physiological parameters

Hepatosomatic (HSI) and splenosomatic (SSI) indices were significantly lower in exposed fish (HSI, $P=0.0001$; SSI, $P=0.0006$) relative to controls. HSIs decreased with increasing SCN^- concentrations ($P=0.0334$), but no dose response was apparent for SSIs ($P=0.3311$). Condition factor was not different between controls and treatment means ($P=0.3107$) and was not affected by SCN^- level ($P=0.5303$).

Fish exposed to SCN^- developed an anemia characterized by decreases in hemoglobin (Hb) and hematocrit (Ht). Hb and Ht treatment means were significantly lower (Hb, Ht, $P=0.0002$) relative to controls. Ht levels showed trends towards decreasing (Ht, P=0.1078) with increased SCN^- concentrations, while Hb levels did not show a dose response (P=0.5669). Plasma total cyanide-reactive substances increased (P=0.0106) with waterborne SCN^-, while plasma T_4 levels were lower (P=0.0284) in treated fish compared to controls and no dose response was apparent (P=0.67), due to the high variability between tanks within treatments (P=0.0421).

Histology

Histological changes were most prominent in the thyroid, with hypertrophy and hyperplasia of the thyroid follicular epithelium in all fish exposed to SCN^-. The number of follicles present in treated fish increased when compared to controls. The changes affecting the thyroid can be best characterized as "diffuse hyperplastic goitre". Control fish had low numbers of large follicles, most filled with eosinophilic colloid, and lined by a low cuboidal or squamous epithelium.

Fathead minnow reproduction study

Juvenile fathead minnows (≈4 months old) were continuously exposed to SCN^- concentrations of 0.05, 1.1, 7.3, 16.6, or 32.6 mg/L for 124 d. Since no secondary sexual characteristics were evident at the beginning of the exposure period, ten fish were later thinned out to 2 males/4 females per tank. After 3 weeks of exposure, spawning substrates were introduced into the test system. Development of secondary sexual characteristics and spawning behaviour were monitored. Reproductive parameters (time to first egg production, number of eggs produced, hatchability) and larval survival and incidence of deformities were monitored. After 124 d, fish were anaesthetized in MS222, and length, weight, and hematocrit were measured. Blood samples were taken by caudal peduncle severance for plasma SCN^- determination by HPLC. Fish were then fixed whole in 10% buffered formalin for routine histological observation.

The NOEC for reproductive performance was between 1.1 and 7.3 mg/L in the water and at about 2.5 mg SCN^-/L in the plasma. Exposure to waterborne SCN^- levels of ≥7.3 mg/L resulted in the development of overt goitre, incomplete sexual maturation, decreased egg production, and increased mortality and time to first spawn.

Embryonic development and larval mortality to 3 d post-hatch were monitored in eggs spawned by adults exposed 0.05 and 1.1 mg SCN^-/L and subsequently exposed to 0.05, 1.1, 7.3, 16.6, and 32.6 mg/L. Treatment effects were determined by split plot ANOVA. Adult thiocyanate pre-exposure level increased percent eyeup, hatch, and eyed eggs to hatch, while decreasing larval mortality and time to hatch. Egg incubation SCN^- concentration had no significant effect on these parameters.

Eggs spawned by adults exposed to 0.05, 1.1, and 7.3 mg/L were reared to adult stages while monitoring reproductive response. Only fish exposed to 0.05 or 1.1 mg SCN^-/L spawned successfully, while fish exposed to 7.3 mg/L matured, but developed overt goitre and did not spawn. Control larvae placed in 16.6 or 32.6 mg SCN^-/L developed overt goitre, exhibited poor growth with complete mortality by 8 weeks.

After the 124 d exposure period, adults exposed to 0.05, 1.1, 7.3, or 16.6 mg SCN^-/L were transferred to SCN^--free water for 30 d and reproductive response was monitored. Eggs were produced by all groups of fish. Time to first spawn increased with SCN^- pre-exposure concentration, with a marginally significant increase in larval deformities in the 16.6 mg/L group.

Rainbow trout SCN^-/CN^- exposure study

Duplicate tanks of juvenile rainbow trout were exposed for 16 weeks to either 40 mg SCN^-/L, 5 mg SCN^-/L, 15 ug CN^-/L, 5 ug CN^-/L, or no toxicant. At the end of 16 weeks, fish were killed by an overdose of anaesthetic (MS222) and weighed. Blood was collected by caudal peduncle severance for hematocrit determination and plasma samples. Plasma SCN^- was determined by HPLC (Brown et al., in preparation) and plasma thyroid hormones by radioimmunoassay. The peritoneal cavity was opened, spleen and liver removed, weighed, and HSIs and SSIs calculated. Thyroid, liver, spleen, kidney and gonad were prepared for routine histological observation as described previously.

Standard ANOVA procedures were used to detect main effects of toxicant exposure. Normality and homogeneity of variance of the data was determined by examination of residuals, and ANOVA was performed on $\log_{10}$ transformed data if these assumptions were violated. *A posteriori* comparison of means was conducted Tukey's HSD (α=0.005).

Exposure to 40 mg SCN^-/L for 16 weeks decreased final body weight, HSI, SSI, and hematocrit compared to all other treatment groups. Plasma T_3 levels were marginally depressed in fish exposed to 40 mg SCN^-/L, but plasma T_4 levels did not appear to be affected, possibly due to the within tank variability. T_3/T_4 ratios were not affected by any treatment. Plasma SCN^- levels of treated were elevated above control levels, where no SCN^- was detected in plasma. Fish exposed to 40 and 5 mg SCN^-/L had mean plasma SCN^- levels of 63.7 and 10.1 mg/L, respectively. Groups exposed to CN^- (15 and 5 ug/L) had lower mean plasma SCN^- levels of 2.21 and 1.14 mg/L, respectively. Histological observations on selected tissues is currently underway.

Preliminary field assessment

Two gold mining regions of northern Ontario were selected as sites for the preliminary environmental health assessment of the impacts of SCN^--bearing effluents on aquatic systems. The two mine sites selected were the Hemlo area, east of Thunder Bay on the north shore of Lake Superior, and Larder Lake, located near Kirkland Lake.

No SCN^- was detected in any of the water samples taken from lakes in the Hemlo sampling area. Although some low level peaks appeared in a few plasma chromatograms, no definitive peaks of SCN^- were found in the plasma of suckers sampled from the Hemlo area. Any indications of plasma SCN^- levels are likely associated with the metabolism of cyanogenic components of the diet, and not related to any waterborne forms of SCN^- or CN^-. These levels of plasma SCN^- are much lower than those found to be associated with goitre development in rainbow trout and would not be expected to result in any interferences with normal physiological processes.

Preliminary assessment of fish population data obtained from Herrick Lake, a lake downstream from the outfall area of the Hemlo mines, showed no apparent adverse effects on white sucker populations. Fish sampled in early September exhibited no gross lesions, had normal gonad development, and many year classes (including juveniles) were present in the sample.

Waterborne SCN^- (1.6 mg/L) was detected near the effluent outfall area of the Kerr-Addison mine in Larder Lake during the spring of 1989, but samples taken in July of the same year did not indicate the presence of SCN^-. Thiocyanate was not detected in water samples from a spawning inflow of Larder Lake (Bear Creek), nor in any water samples taken from the control site, Raven Lake. Plasma samples of suckers taken from both Larder and Raven Lakes did not reveal the presence of any significant amounts of SCN^-.

Preliminary observations of thyroid tissues sampled from suckers indicates no apparent differences in thyroid tissue structure between fish sampled from test or control lakes in the Hemlo mining area. Fish sampled from Larder Lake appear to have fewer thyroid follicles than fish sampled from the control lake, Raven Lake, in the Kirkland Lake area. However, thyroid tissues from Raven Lake appear very similar in structure to those taken from fish in the Hemlo area.

DISCUSSION

The major consequences of the chronic sublethal exposure of rainbow trout to SCN^- are changes in thyroidal morphology characterized by a diffuse, hyperplastic goitre, alterations in plasma thyroid hormone, deformities in the cranial cartilage, and an anemia characterized by reduced hemoglobin, hematocrit, and splenosomatic indices. Chronic exposure to 5 mg SCN^-/L, 5 ug CN^-/L, or 15 ug CN^-/L elevated plasma SCN^- levels above control values, but did not result in the development of any of the signs characteristic of chronic SCN^- toxicity in rainbow trout.

Chronic exposure to SCN^- resulted in the development of overt goitre and reduced the expression of secondary sexual characteristics, spawning behaviour, and egg production in fathead minnows. The no observed effect concentration (NOEC) for egg production and spawning behaviour was between waterborne SCN^- levels of 1.1 and 7.3 mg/L. In terms of an internal body residue, depressed reproduction occurred in fathead minnows at plasma SCN^- levels of about 2.5 mg/L.

Sublethal SCN^- toxicity in rainbow trout and fathead minnows appears to involve thyroid function, as seen by histological evidence regarding goitre development, alterations in plasma thyroid hormone levels in trout, deformities in cranial cartilage development, and suppression of secondary sexual characteristics and egg production in mature fathead minnows. The dramatic reduction in egg production observed in fathead minnows at waterborne SCN^- concentrations between 1.1 and 7.3 mg/L appears to be the most sensitive indicator of SCN^- toxicity. Fertilization rates and larval growth and survival were less sensitive indicators, with a NOEC between 7.3 and 16.6 mg SCN^-/L. The development of overt goitre in fathead minnows at 7.3 mg SCN^-/L, but not in rainbow trout exposed to levels as high as 120 mg SCN^-/L may indicate differences in the metabolism of SCN^- between species.

Exposure of rainbow trout to sublethal levels of CN^- resulted in increased plasma SCN^- levels, but not to a level that resulted in an expression of the signs of chronic SCN^- toxicity.

Based upon the response of fathead minnow and rainbow trout to chronic SCN^- exposure, a water quality criterion of not greater than 1.1 mg SCN^-/L, the NOEC for reproduction in the fathead minnow, is suggested.

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BP5

ZOOPLANKTON COMMUNITIES AND WATER CHEMISTRY OF SUDBURY AREA LAKES: CHANGES RELATED TO pH RECOVERY.

A. Locke and W.G. Sprules, Dept. of Zoology, University of Toronto, Erindale Campus, Mississauga, Ontario, L5L 1C6.

Lake acidification related to smelter emissions has been recognized in the Sudbury area since the study of Gorham and Gordon (1960). Studies conducted in Sudbury area lakes in the early 1970's (Sprules 1975, Roff and Kwiatkowski 1977, Keller 1981) showed pH to be a major determinant of zooplankton community structure, so that acidified lakes contained a community of fewer species than lakes of circumneutral pH. Above pH 5.0, zooplankton communities contained 9 to 16 species, with 3 or 4 dominant species. Below pH 5.0, only 1 to 7 species were present, with only 1 or 2 dominant species (Sprules 1975). Compared to unacidified lakes in northwestern Ontario, Sudbury area lakes contained very simple zooplankton associations in the 1970's.

Acidic atmospheric emissions in the Sudbury area have declined in recent years. Sulfur dioxide emissions from local smelters averaged 2.2 million tonnes/year between 1950 and 1972, 1.41 million tonnes/year between 1973-1977, and 0.68 million tonnes/year in 1979-1985 (Dillon et al 1986). In response to this reduction in acidic emissions, recovery from pH stress has begun in Sudbury area lakes. The term "recovery" is used here in the sense of a significant increase in pH and/or a decrease in metal concentrations, and does not necessarily imply a return to the pre-acidified state.

A 1981 survey of 249 northeastern Ontario lakes found that many Sudbury area lakes were still acidified, and that community structure of these lakes resembled that described for acidified lakes in the surveys of the 1970's (Keller and Pitblado 1984). The objectives of our study are to determine whether zooplankton community structure in Sudbury area lakes has changed relative to previous surveys, and if so, to investigate rates of plankton recolonization and direction of community change. We resampled 47 lakes in the La Cloche Mountain region southwest of Sudbury, which had been previously sampled by Sprules (1975). These data will be combined with data from 45 other Sudbury area lakes sampled by W. Keller (Ont. Min. of Envt., Sudbury office) in 1974-1976, 1981-1983 and 1988.

Zooplankton and water chemistry samples were collected from 47 lakes in the La Cloche Mountain region in August 1990. Preliminary results indicate that pH has increased by up to 1.6 pH units relative to 1971-1973 values. Zooplankton results will be presented at the conference. Zooplankton will be judged to be recovering if recolonization by species not present in earlier samples has occurred, decreased dominance by acid-tolerant species is observed and/or if community composition of previously acidified lakes has shifted to resemble that of circumneutral lakes.

BP6

THE RELATIVE EFFECT OF INDIVIDUAL ENVIRONMENTAL FACTORS ON INDICATOR BACTERIAL SURVIVAL; **E. Harris, Lake Simcoe Region Conservation Authority, Newmarket, Ontario, L3Y 4X1.**

INTRODUCTION

Indicator bacterial survival in the water column and bed sediments of 3 rural streams was investigated by the Lake Simcoe Region and Metropolitan Toronto and Region Conservation Authorities between 1987 to 1989 (Harris and Walters, 1989). Bacterial die-off rates in water and sediment were shown to vary between streams, and within a single stream course, due to variations in chemical and physical characteristics. Seasonal variations in water temperature were shown to have an effect on survival. The rate of bacterial die-off moderately increased during summer months and declined in winter. In contrast, nutrient levels appeared to enhance bacterial survival, however the relationship was not well correlated.

Similar influence of these factors on bacterial longevity has been observed in other insitu studies. Unfortunately, under field conditions, the effect of any one factor, or combination of factors cannot be isolated since several changes are occurring simultaneously, and cannot be controlled. For this reason an invitro study of the relationship between water column bacterial decline and environmental conditions was initiated in October, 1989. The study was designed to provide die-off information from controlled laboratory experiments, which would aid in the interpretation of field data collected by the Conservation Authorities.

Laboratory experiments have been used previously to determine the effect of various factors on bacterial die-off. In this study, the effect of water temperature and chemical parameters such as: Dissolved organic carbon (DOC), total kjeldahl nitrogen (TKN), nitrates (NO_3), nitrites (NO_2), ammonia (NH_4), and phosphates (PO_4) was assessed using small aquaria and membrane diffusion chambers containing cultures of indicator bacteria.

METHODS

The control cultures of E. coli (EC) and P. aeruginosa (PSA) used in the experiments were isolated weekly from cow faeces and sewage. Broth cultures of EC and PSA were centrifuged, and diluted 10 fold to a concentration of 10^3 in filter sterilized well water prior to injection into the chambers.

The well water had been selected, based on chemical test results, as a clean source, exhibiting low to trace levels of the various chemical parameters. Filter sterilization using a 0.2 micron Millipore filter was found to be preferable to autoclaving the water, as this latter method results in a delayed die-off effect (Harris and Walters, 1989).

Commercial 5 gallon aquaria were installed in large incubators, and filled with 9 litres of filter sterilized well water. The tanks were continuously aerated during the experiments by pumping air into the water via plastic tubing connected to aquarium pumps.

Both control and test tanks were used for each experiment. Test tanks were prepared by increasing concentrations of individual chemical parameters, such as DOC or NO_3 to levels observed in fresh water streams receiving variable pollution impacts. This was accomplished by adding pre-calculated amounts of appropriate media such as manure or sodium nitrate to the tanks. Control tanks contained only filtered well water.

Fresh water and chemicals were added to the tanks every 2 days during the experiments. The tank water was sampled for chemical analysis at the start of each experiment, after each water change, and at the end of the experiment. Samples were submitted to the Ministry of the Environment (MOE) for analysis of all the test parameters, as well as, conductivity, turbidity, and pH.

For the water column experiments, triplicate diffusion chambers were filled with the diluted EC and PSA suspensions, and then placed into the aquaria. Separate chamber sets were used for each control, as PSA is somewhat inhibited by the presence of EC in diffusion chambers (Harris and Walters, unpublished data). Bacterial concentrations were measured over a six day period by daily withdrawing 3 mL samples from the chambers, and analyzing these by membrane filtration for EC and PSA. All analyses were performed according to MOE methods.

Four replicate experiments examining the effect of different DOC concentrations on bacteria survival were run at 3 temperature regimes: 4°c, 10°c, and 20°c. Triplicate tests assessing the effect of other chemicals on survival were run at 20°c only.

In sediment survival experiments, chambers were filled with 50 grams of a filter washed mixture of fine sand and bentonite clay, and then inoculated with 5 mL of the diluted EC or PSA culture. Inoculated chambers were then placed in the aquaria . Only the effect of increased DOC on sediment bacterial survival was determined by duplicate experiments at 10°c and 20°c. The experiments were conducted over a 10 day period by daily removing chambers and analyzing the sediments for EC or PSA using MPN procedures specified by the MOE.

Data from the survival runs was analyzed by statistical tests. Bacterial survival rates were computed by linear regression analysis of the bacterial concentration in each chamber with time. Comparison of the die-off rates between control and test groups was performed by single factor anovar analysis. The relationship between water column bacterial survival, water temperature and DOC was also assessed by linear regression analysis.

RESULTS

Water column and sediment bacterial die-off rates determined under different temperature and chemical treatments are presented in Figures 1 and 2. The rates shown are a geometric mean average of data from all runs. Test groups 1 (Figs. 1 and 2) refer to experiments utilizing moderate increases in the various chemicals, while test groups 2 denote experiments examining the effect of large increases.

As seen in Figure 1, the die-off rate of EC in the control tanks was found to increase with increasing water temperature. Regression analysis of EC die-off with temperature showed a significant, but not strong positive correlation ($r = +.584$). Elevating DOC levels in the water counteracted the effect of temperature, causing die-off to decrease dramatically (Fig. 1). EC die-off rates showed a strong negative correlation with DOC ($r = -.705$). However, anovar analysis revealed that significant differences in the die-off rates between control and test DOC tanks occurred only at 20°c (5% probability level).

PSA in contrast, exhibited an elevated survival response to increasing temperature ($r = -0.734$). Previously, this organism was found to grow in well water at temperatures of 15°c or higher (Harris and Walters, unpublished data). Increasing DOC levels accentuated this growth response. Significant differences in die-off rates between control and test tanks occurred at all three temperatures.

Magnifying the concentration of NH_3, NO_3, TKN, and PO_4 in aquaria water at 20°c, produced almost no effect on the die-off rates of EC (Fig. 1). Residual chloride caused a decrease in die-off when increased moderately possibly due to the establishment of more favourable osmotic conditions for the organism. Elevating NO_2 concentrations resulted in an increased die-off response. NO_2 may be slightly toxic to the organism at high levels, and under these conditions.

PSA die-off rates varied in response to elevated NH_3, NO_3, NO_2, TKN, and PO_4 (Fig. 1). Die-off was not observed in the NH_3 and NO_2 control and test tanks. Invitro PSA die-off response is variable at 20°c, and it is not uncommon for regrowth to occur. However, the regrowth of PSA in the NH_3 test tanks was more pronounced than in the control tanks. Increasing levels of TKN and PO_4 appeared to cause a decrease in die-off, while elevating residual chloride levels had no effect. Anovar analysis of the data from these experiments did not detect any significant differences in the die-off rates between control and test tanks despite these observed trends.

Both EC and PSA exhibited somewhat increased die-off rates in sediments under elevated DOC conditions (Fig. 2). This observation is not supported by field die-off data. Unfortunately, anovar analysis could not be performed on the sediment survival data due to lack of sufficient replication. It is therefore difficult to determine if the observed increases in die-off were significant.

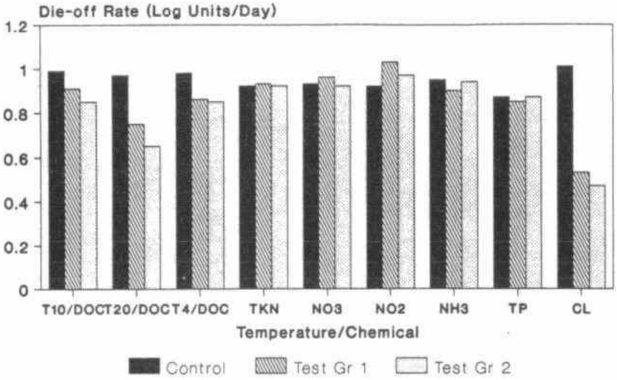
Adsorption of the bacteria onto the clay may be affected in some way by the increased DOC content, through changes in pH or the surface charge of the clay particles. Whether the affect is increased adsorption, leading to reduced bacterial recovery and a false die-off effect, or decreased adsorption, resulting in a loss of the clay's protective action, is unknown, and beyond the scope of this study.

CONCLUSIONS

Bacterial survival response is heightened by elevated levels of DOC in water. The survival phenomenon is most pronounced at warmer temperatures, but occurs under colder conditions as well. Reducing inputs that cause increased DOC levels in streams may help to increase bacterial die-off, and thereby lessen the biological pollution impact on downstream areas. DOC analysis should be included in routine monitoring tests.

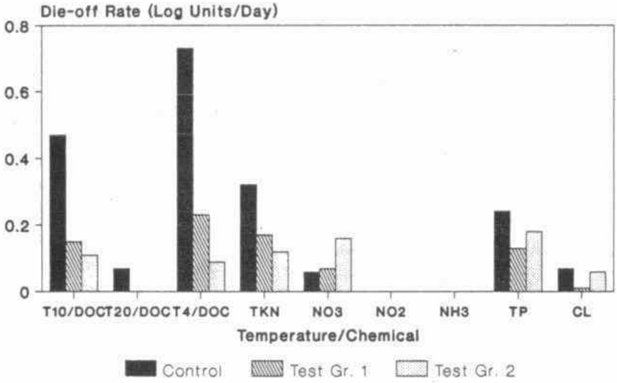
Figure 1

THE EFFECT OF TEMPERATURE AND NUTRIENTS ON E. COLI SURVIVAL



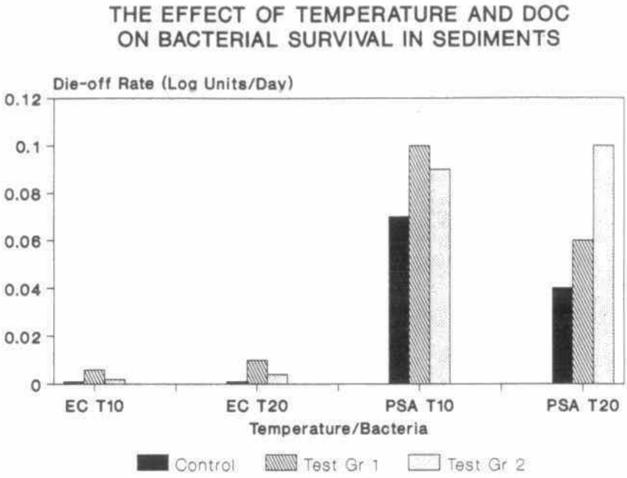
T = Temperature in degrees celsius
NO3/NO2/NH3/TKN/TP/CL = 20 degrees C

THE EFFECT OF TEMPERATURE AND NUTRIENTS ON P. AERUGINOSA SURVIVAL



T = Temperature
NO3/NO2/NH3/TKN/TP/CL = 20 degrees C

Figure 2


THE EFFECT OF TEMPERATURE AND DOC
ON BACTERIAL SURVIVAL IN SEDIMENTS
Die-off Rate (Log Units/Day)
0.12
0.1
0.08
0.06
0.04
0.02
0
EC T10
EC T20
PSA T10
PSA T20
Temperature/Bacteria
Control
Test Gr 1
Test Gr 2

BP7

THE EFFECT OF FARM LIQUID WASTE APPLICATION ON RECEIVING WATER QUALITY

D.M. Dean* and M.E. Foran, Ausable Bayfield Conservation Authority,
Exeter, Ontario N0M 1S7.

Previous studies by the Ausable Bayfield Conservation Authority (Balint 1985) and the Ontario Ministry of the Environment, Southwestern Region (O.M.E. 1984) established that in some cases the land application of liquid manure causes bacterial and chemical contamination of field tile drains. The effluent from those tile drains may result in contamination of receiving streams and ultimately beach closures. The primary objectives of this current study are to determine how soil structure, soil moisture and rate of application influence the impact of land application of liquid manure on tile drain water quality.

Previous research on bacterial movement through soil columns, including studies by Gerba *et al.* (1975), Smith *et al.* (1972), and McCoy (1969), indicated that soil was an efficient filter for bacteria. On the contrary, and in support of this study, Evans and Owens (1972) found a 30-900 fold increase in fecal bacteria concentration in the tile effluent from a sandy clay loam pasture field within two hours of spreading liquid manure. A one time observation by Patterson *et al.* (1974) found the water from 1.5 m deep drains in a plowed field to be cloudy and foul smelling within 30 minutes after a 5mm (50,000 Lha^{-1}) application of liquid manure.

Thus far, 11 liquid manure spreading events have been monitored on a total of 5 different soil types, under a variety of field conditions, in Huron and Perth Counties, Ontario. Table 1 gives a summary of each of the manure spreading events including the rate of manure application, a brief description of the field conditions and changes in bacterial water quality. Participating farm operators and/or custom applicators were requested to spread the liquid manure as they would normally. The irrigation method of spreading was used for 10 of the manure applications, while a tank spreader with manure broadcast on the ground was used for the remaining one. Changes in the concentrations of bacteria and nutrients in the soil underlying the area of manure application were monitored in addition to changes in the tile drain water quality. Bacterial parameters tested for in the manure, tile drains and soil included, fecal coliform, fecal streptococcus, and *Escherichia coli*. For 9 of the manure applications the biotracers; nalidixic acid resistant *Escherichia coli* (E.C.(N.A.)) and rifampicin resistant *s. faecalis* (F.S.(R.I.F.)), were introduced with the liquid manure to trace bacterial movement in the soil and water. These biotracers are easily detected in water and soil and are not normally present in the natural environment.

For 7 of the 11 manure spreading events (numbers 1, 3, 5, 8, 9, 10, and 11) (see Table 1) water quality degradation was observed within 2 to 7 hours following the initiation of spreading. It is believed that soil macropores provided pathways for the manure to travel to the tile drains. Soil moisture is also believed to have played a role since contamination of tile drains only occurred when there was some tile flow prior to spreading. Event numbers 2, 4, 6, and 7 experienced little or no contamination of the tile drains. For numbers 2 and 4, low levels of contaminants were present when tile flow resumed. For #6 little contamination of

Table 1: Summary of Each of the Manure Application Runs

Event #	Date	Soil Type	Tile System and Spacing	Crop Rotation	Ground Cover and % Residue$^+$	Tile Flow	Rate of Application L ha^{-1}	Comments
1	May '89	Perth clay loam	systematic 15 m	corn/bean/ wheat	fall plowed 6%	Yes	76,500	- 3400 fold increase in bacti. conc. in 2 hours
2	Aug '89	Perth clay loam	systematic 15 m	corn/bean/ wheat	wheat stubble 95%	No	140,700	- contamination (low) delayed until tile flow resumed
3	Sept '89	Perth clay loam	random	corn/barley /hay	corn silage stubble 57%	Yes	93,000	1600 fold increase in bacti. conc. within 4 hours
4	Oct '89	Brookston clay loam	systematic 15 m	soybean/ corn	soybean residue 76%	No	56,000	- contamination (low) was delayed until flow resumed
5	Nov '89	Wauseon sandy loam	systematic 15 m	soybean/ corn	soybean residue 78%	Yes	54,000	- 1000 fold increase in bacti. conc. within 6 hours
6	May '90	Listowel silt loam	systematic 15 m	soybean/ corn	fall plowed 6%	Yes	36,000	- 200 fold increase in bacti. conc. within 5 hours
7	Jun '90	Perth clay loam	systematic 15 m	corn/bean/ wheat	seed bed prepared 1%	Yes trickle	111,000	- slight increase in bacterial concentrations but not significant
8	Jul '90	Perth clay loam	random	hay/corn/ grain	hay 93%	Yes V.High	100,000	- 30 fold increase in bacti. conc. within 20 minutes
9	Aug '90	Perth clay loam	systematic 15 m	corn/bean/ wheat	wheat stubble 94%	Yes trickle	106,000	- 45,000 fold increase in bacti. conc. in 2.5 hours and increased tile flow
10	Sept '90	Listowel silt loam	systematic 15 m	corn/bean/ wheat	wheat stubble 94%	Yes trickle	44,300	- 30,000 fold increase in bacti. conc. and increased tile flow
11	Sept '90	Huron clay loam	systematic 15 m	corn/bean/ wheat	wheat stubble 96%	Yes	72,000	- 1,000 fold increase in bacti. conc. in 2 hours

the tile drains occurred on the day of spreading, however, after a 15 mm rainfall the following day, the tile drains were contaminated. In #7, in which no significant contamination resulted in the tile drain water, manure was spread on ground that was recently prepared for seeding of white beans. This cultivation may have destroyed the continuous root or pore channels in the surface soil horizon.

At each manure application site, soil bacteria, including the biotracers, were measured in the soil profile at three depths: 0-10 cm, 30-35 cm, and 45-50 cm (1989), 70-75 cm (1990). Figure 1 shows the concentration of both fecal coliform bacteria and the introduced (FS(RIF)) bacteria at various depths in the soil, before and after spreading, expressed as # of bacteria per 100 g of soil. This profile, which is from event #2 is typical of other events, with the exception of #7 where there was virtually no movement of bacteria through the soil column. Biotracer results confirmed that contamination from the spread manure reached the tile drain water. Figure 2 shows tile drain concentrations of fecal coliform and the introduced (FS(RIF)) over time for one of the spreading events.

Figure 1. Soil Bacteria Concentrations
Event #2 - August 1989

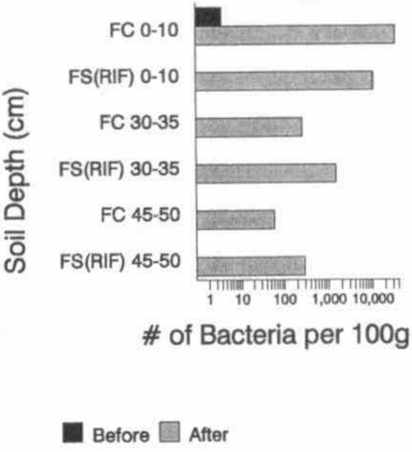
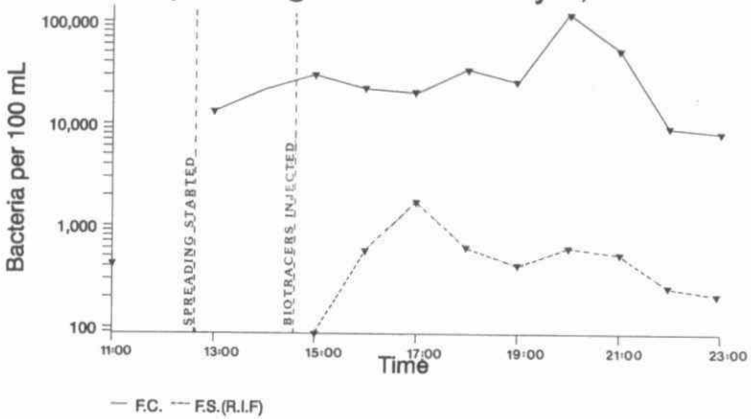


Figure 2. Drain Bacteria Concentrations
Spreading Event #8 - July 9, 1990



It appears that the four major factors influencing the impact of land application of liquid manure on tile drain water quality are; the presence of established continuous macropores (root/animal channels and structural cracks), tile drain flow at the time of spreading, rainfall shortly following manure application, and the rate of application.

This study was subject to some scheduling difficulties in 1989 and 1990 due to weather and crop stage. It is anticipated that manure spreading events will be monitored two more times in 1990. Future research should focus on the impact of tillage prior to manure application since macropore flow appears to be the dominant factor in the transport of manure to tile drains.

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[+] Percent Residue Cover - A 30.5 m rope with markings every 30.5 cm is laid diagonally to the direction of cultivation. The percent residue is determined by counting the number of times that residue is present at the 30.5 cm markings. The minimum residue size is 3.8 cm by 0.3 cm.

BP8

STATISTICAL ASSESSMENT OF MULTIVARIATE ORDINATION TECHNIQUES FOR ZOOBENTHIC COMMUNITIES AND WATER CHEMISTRY FOR LAKES FROM CENTRAL ONTARIO. Donald A. Jackson* and Harold H. Harvey, Department of Zoology, University of Toronto, Toronto, Ontario M5S 1A1

Researchers studying ecological communities or environmental impact assessment frequently must assess data sets comprising large numbers of sampling sites, species, and environmental variables. The large number of pairwise comparisons of variables makes the use of simple correlation analysis of limited use. With increasing frequency, researchers employ some method of multivariate statistical technique such as principal component analysis (PCA) or cluster analysis. Many of these methods are applied indiscriminantly without regard for the underlying assumptions of the methods and the characteristics of the data. For example, water chemistry variables are often non-linearly related yet researchers use methods requiring linear relationships (e.g. PCA, canonical correspondence analysis). The implications of using these methods are still poorly recognized.

When using any of these methods, an underlying assumption of the techniques is that there are non-random patterns among the sites or variables. Multivariate analyses are used to summarize these methods into a reduced number of dimensions. Unfortunately, with field-collected data, the dimensionality of the patterns is unknown. It is important to recognize the dimensionality of the data otherwise one risks discarding important information associated with unutilized multivariate components or interpreting nonsignificant components as being important. We are examining various traditional measures of assessing the dimensionality as well as developing alternative methods employing bootstrapping (statistical resampling) techniques.

More comprehensive measures of the concordance between ecological communities and their corresponding environmental conditions are being developed. Traditional approaches have included correlating community-based multivariate axes with environmental variables (again leading to excessive numbers of correlations and the associated inflated Type I error) or methods such as canonical correlation analysis which assume linear relationships among and between the species data and the environmental data. We have developed a multivariate measure testing the concordance between benthic invertebrates, fish species compositions, water chemistry, lake morphometry, and spatial arrangement. **PROTEST** is a multivariate **PRO**crustean **TEST** based on a least-squares measure of the goodness-of-fit between two data sets with the subsequent probability determined using a randomization test. The rationale and use of **PROTEST** will be discussed in our presentation.

BP9

GEOCHEMICAL ALTERATION OF ROAD DE-ICING CHEMICALS BY SUB-SURFACE ROCK-SOIL-WATER INTERACTIONS.

K.W.F. Howard* and J.Haynes, Groundwater Research Group, University of Toronto, Scarborough Campus, Scarborough, Ontario M1C 1A4

Introduction

Road de-icing chemicals are one of the most serious causes of groundwater pollution in Canada. Applied to roads and highways throughout southern Ontario and many other Canadian Provinces, the chemicals (NaCl and $CaCl_2$) are easily mobilized by rain and meltwaters. As a result, typically 50% of annually applied road de-icing chemicals are flushed from the catchment by surface waters, with the remaining 50% infiltrating slowly through the unsaturated zone to the water table where it threatens to cause widespread degradation of groundwater quality. An ongoing study by the Groundwater Research Group at the University of Toronto plans to develop a series on numerical models that will predict the environmental fate of these chemicals and thereby recommend procedures that will minimize environmental impact.

While the predictive models should deal adequately with the fate of the chemically conservative chloride ion, the predicted behaviour of Ca and Na will depend on a knowledge of the interactions between these ions and the shallow sub-surface soils and sediments. Soil water in the unsaturated and saturated zone is usually in equilibrium with the ions adsorbed on the soil particles and organic matter. As precipitation or run-off infiltrates through the soil, its composition changes to reach equilibrium with the soil by exchange between the adsorbed and free water ions. When road salt laden waters enter the soil during winter or early spring, the sodium ion, which is the dominant cation species, exchanges with the cations adsorbed in the soil (mainly calcium). By the time infiltrating water reaches the water table, its original cationic composition will have been changed by a series of soil-water interactions, the magnitude of the change depending on the soil or rock type, the thickness of the unsaturated zone and the chemistry of the preceding infiltrating waters. During the summer, repeated infiltration of salt-free water will reverse the exchange process and remove the weakly adsorbed sodium, to near background concentration levels. Studies in Britain showed that sodium adsorbed during winter salting was removed from the upper 50 mm of roadside soils prior to the onset of the following winter (Thompson, et. al. 1986)

Below the water table the equilibrium chemistry of salt-laden and salt-free waters will continue to evolve, influenced by the ion exchange equilibrium. Studies in a road salt contaminated shallow aquifer by Killey and Devgun (1987), identified changes in the chemistry of a salt plume. Near the source of the plume, calcium concentrations were at background levels but sodium was much higher (Na:Ca ratio approximately 3). Further downgradient, the equilibrium had changed to achieve a Na:Ca ratio of 1, typical of background waters. However, both sodium and calcium concentrations were now above background levels.

Laboratory Experiments

Current research described here is addressing the role of rock-soil-water interactions on modifying the chemistry of the infiltrating waters through a series of laboratory experiments. Two types of experiment are being carried out, both involving salt solutions prepared by dissolving commercially available road de-icing salts in simulated precipitation. For both types of experiments, cation exchange capacity and exchangeable cations are determined respectively by using sodium acetate and ammonium acetate saturation to extract ions, and by using atomic absorption/flame emission to analyse for the major cations. In the first type of experiment, batch tests are being performed using sandy and silty soils with varying organic content, clay content and carbonate content. Soil samples are saturated alternately with salt solutions at varying concentrations and with simulated rainfall. The supernatant is collected and analysed for major ions. Exchangeable major cations are determined for the treated soil. The ratio of Na:Ca occupying exchange sites is determined for different treatments.

The other type of experiment uses a simple soil column to examine the changes in water chemistry and adsorbed cations resulting from infiltration of salt water through an unsaturated soil. Soil cores, averaging 80 cm in length, are obtained from an urban park, by hammering 55 mm diameter acrylic tubes into grassed alluvial soils. Except for some minor compaction, the soil cores, when visually compared with the soil profile exposed in an adjacent test pit, are relatively undisturbed. Table 1 lists the properties of the soils used in the first infiltration series. The soil is a silty fine sand grading into a medium sand below 0.85 m. The B horizon is enriched in clay (15% ave. versus 9% ave. and 3% in the A and C horizons respectively). In the laboratory, the soil core was infiltrated with a series of 250 ml aliquots of simulated rainfall containing either no salt or salt at various concentrations. The composition of the aliquots was designed to imitate the pattern of a soil receiving road run-off during the salting season and shortly after. The core was gravity drained, and each infiltration event took 36 - 48 hours to complete. The effluent from each infiltration event was analysed for major cations to examine changes in the infiltrating water. At the conclusion of the infiltration series, the soil core was extruded and sampled in 60 mm sections. Each section was sub-sampled, from the centre, edge, and across the column to identify any channelling during infiltration. (No channelling was visible during infiltration; the wetting front advanced relatively uniformly down the column.) Moisture contents were measured. Exchangeable major cations were determined for 12 representative samples and compared with ratios of exchangeable ions prior to testing.

Experimental Results

The experimental results reveal that the cationic constitution of the road salt solutions can be significantly altered by rock-soil-water interactions. Most significantly these changes take place in the organic soil A horizon. The B and C soil horizons contribute less actively to the cation exchange process. The experimental results are consistent with the basic exchangeable cation characteristics of the shallow soils and sediments; the findings are also consistent with the chemical character of groundwaters known to be contaminated by road de-icing chemicals.

Table 1 Soil Properties - Soil Core Sampling Site

Horizon	Zone	Depth m	Texture	Organic Matter wt. %	Ratio Exchangeable Na:Ca
A	A1	0 - .21	silty sand	4.7	0.01
	A2	0.21 - 0.38	silty sand	3.8	0.01
B	B1	0.38 - 0.45	clayey silty sand	1.7	0.03
	B2	0.45 - 0.59	clayey silty sand	2.2	0.04
C		0.59 - 0.85	silty sand	0.6	0.1

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BP10

STANDARDIZED REARING MATERIALS AND PROCEDURES FOR HEXAGENIA, A BENTHIC BIOASSAY ORGANISM: COMPARISON OF SEDIMENT TYPES

Elizabeth C. Hanes, Jan J.H. Ciborowski and Lynda D. Corkum
Department of Biological Sciences
University of Windsor
Windsor, Ontario, N9B 3P4

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ABSTRACT

All life stages of the aquatic mayfly Hexagenia have been used extensively for biomonitoring/bioassay applications. However, use of larvae for toxicokinetic studies and bioassay procedures is limited by lack of standardization in control sediments. A synthetic medium suitable both for rearing and for laboratory contaminant assessment must 1) promote high larval survival and rapid growth; and 2) be free from contaminants of concern.

To characterize sediments most suitable for larval growth, we collected sediments from six field sites: Anchor Bay, Lake St. Clair (ANC); Balsam Lake (BAL); Cook's Bay, Lake Simcoe (COO); Honey Harbour, Georgian Bay (HON); Lake Nicolet, St. Marys River (NIC); and Saginaw Bay, Lake Michigan (SAG). A synthetic laboratory standard (STND) sediment (2:1 dry wt. potting soil:potters clay) previously used for successful rearing (<20 % mortality) was compared to field samples. All sediments were dominated by silt/clay. Organic content ranged from 2 % (ANC and NIC) to 28 % (STND).

One-day old larvae were inoculated into growth tanks (7 larvae per 63 cm^2 tank) containing one of the 7 sediment types for 90 d and until adult emergence (n = 5 replicates/ sediment type/ time trial). Mean head width (HW) and relative mortality were determined for each tank. After 90 d growth, larval survival in SAG, NIC, COO and STND (55-85%) was significantly higher than in ANC, BAL, HON and SAG (25-55%) sediment ($P< 0.01$). Larvae grown in HON and SAG sediments had attained the largest size. BAL, STND and ANC sediment supported the smallest larvae ($P < 0.001$). Other trials that rear larvae to emergence are still in progress.

Two larval substrate preference experiments were conducted. Blocks of the 7 sediment types were placed in an aquarium to form a grid of 49 cells. Eight larvae/ cell were added and allowed to move freely among cells. After 7 d, SAG, ANC, COO and HON contained significantly more larvae then other sediments ($P < 0.001$). STND sediment harboured the fewest larvae.

Since Saginaw Bay sediment is the most conducive to growth and survival of larvae, we are altering constituents of our standard sediment using diatomaceous earth, potter's clay and potting soil to more closely mimic the preferred sediment. The general utility of synthetic sediment in bioassay procedures is being examined by comparing responses of Hexagenia larvae in the standard sediment to growth in field-collected contaminated sediment.

1. INTRODUCTION

Larvae of Hexagenia mayflies are important field and laboratory test organisms. They have been recommended as a standard for evaluating toxic effects of contaminated sediments (International Joint Commission 1987; Lomas and Krantzberg 1988). These organisms are a common food source for many fishes and thus may play a significant role in contaminant transfer from sediments to other trophic levels. Hexagenia have been used extensively for biomonitoring/bioassay applications in egg (Friesen 1979), larval (Fremling 1967; Henry et al. 1986; Bedard 1990) and adult (Kovats and Ciborowski 1989) developmental stages. However, use of Hexagenia for toxicokinetic studies, bioassay procedures and field biomonitoring is limited by lack of standardization in control sediments and availability of test animals.

Various sediment bioassay and biomonitoring techniques assume that variation in test organism survival, growth and/or ultimate contaminant burden directly reflect the concentration and toxicity of contaminants in the sediment. Response differences between contaminated and uncontaminated site-collected treatments (sediments) presumably reflect the influence of the contaminants alone. We propose that comparing these treatments with a culture-sediment control permits one to ascertain the extent to which on-site sediment effects result from inappropriate or suboptimal physical sediment characteristics. Accordingly, we are developing protocols directed towards providing suitable standardized substrate and rearing conditions for larvae of Hexagenia.

The objectives of our study were to make available a continuous supply of eggs suitable for laboratory rearing, and to develop and determine the effectiveness of standard sediment and feeding regimes suitable for promoting rapid, synchronous growth of larvae of Hexagenia, using easily acquired materials free of organic and inorganic contaminants. In this report, we outline:

1) Collection and cold-storage maintenance of genetically consistent Hexagenia egg stocks from Lake St. Clair emergent populations. This material is maintained for distribution on request to individuals/organizations requiring research/assay specimens.

2) Synthesis of a sediment composed of commercially available materials of texture and composition suitable for promoting contaminant-free development of newly-hatched larvae of Hexagenia to maturity in the laboratory.

3) Comparison of larval Hexagenia growth (relative to synthesized sediment) in natural sediments from habitats especially suitable for Hexagenia development with growth in the synthetic sediment.

2. MATERIALS AND METHODS

2.1. Study animals and rearing conditions

2.1.1. Collection of study animals and maintenance of eggs

Eggs were collected in the summers of 1989 and 1990 from females emerging from Lake St. Clair (42°20'N 82°57'W). Adult females were collected in late June and early July using portable ultraviolet light traps (Kovats and Ciborowski 1989). Approximately 6.5 million eggs were obtained from a total of ca. 1600 female imagoes in each year. Taxonomic analyses of males collected at the same time suggest that approximately 67 percent of imagoes were H. limbata (Serville) and 33 percent were H. rigida McDunnough (n=250). Adult females cannot be identified to species.

Eggs from groups of 20 or more females were amalgamated into polyethylene bags containing aerated, distilled water. All eggs were cooled in a stepwise fashion to 8°C in 4°C decrements (Friesen 1981) and stored to provide a year-round supply of stock material.

To evaluate the possible influence of overwintering eggs on delayed recruitment into natural populations, the effect of cold storage was examined. Eggs collected in 1989 were used to estimate viability and to determine whether a proportion of eggs required a period of cold-storage prior to hatching that may contribute to subsequent size variation observed in natural larval populations.

At the time that eggs were returned to the laboratory after collection, batches of approximately 100 eggs were removed from their bags. Half of the eggs (n=50) were placed in covered petri dishes at room temperature while the other half were cooled to 8°C in 4°C decrements and stored under refrigeration. The eggs kept at room temperature were monitored daily for two weeks. As larvae hatched, they were removed from the petri dish and enumerated. The unhatched eggs were then left at room temperature and examined every few days for two months (D. Giberson, University of Manitoba, pers. comm.). At the end of this period (12 Sept 1989) they were placed into cold storage (8°C). On 11 January 1990, these eggs, in addition to the eggs originally put in cold storage were warmed to room temperature to monitor hatch over a further 3 month period.

2.1.2. Larval rearing conditions

Animals were reared in containers under laboratory conditions as outlined by Hanes (1989). Two-L glass jars (Lomas and Krantzberg 1988) are equally suitable containers. One-day-old larvae were inoculated into appropriate sediments and maintained at densities and feeding schedules previously determined to maximize growth and survival (Hanes and Ciborowski 1989). Rearing chambers consisted of either 500-mL or 1-L styrofoam or plastic tubs (7 larvae 63 cm^{-2} = 1000 larvae m^{-2}; Hanes 1989) or 2-L glass jars (Lomas and Krantzberg 1988). Containers were aerated using the multiple-bank system of Corkum and Hanes (1989). Lighting was provided from incandescent and fluorescent sources, timer-regulated to correspond to a 16:8 L:D photoperiod. All rearing chambers were maintained at room temperature (21-24° C). This temperature produces higher survival rates and greater size at maturity among laboratory-reared specimens than other temperatures (Wright and Mattice 1981a). Values of dissolved oxygen, conductivity and pH were monitored at regular intervals throughout all experiments. Larvae were fed an aqueous mixture of ground Tetramin® fish food, aflalfa flour and baker's yeast (modifed from M.G. Henry, Univ. Minnesota, pers. comm.) applied to the water surface as an aerosol every 3-4 days (20 µg dry wt./cm^2/d ; Hanes, 1989).

2.2. Artificial sediment synthesis

Previous workers evaluating growth, behaviour and ecotoxicology of burrowing mayflies have used locally collected natural sediments from purportedly uncontaminated regions (Landrum and Poore 1988, Bedard 1990). M. Friesen (pers. comm.) proposed using plant potting soil as a rearing medium for Hexagenia rigida larvae. M. Henry (pers. comm.) found that Hexagenia limbata grew well in sediments composed of a mixture of potting soil and Lake St. Clair clay. We previously achieved excellent rearing success (>90 percent survival) using a mixture of 2 parts potting soil and 1 part potter's clay (ratios based on dry weight) (Hanes and Ciborowski 1989).

Potting soil (Zehr's "No Name" Potting Soil®) was air dried and passed through a No. 10 (1-mm) sieve to remove large clumps of organic material. An appropriate (moisture corrected) quantity of Terra Cotta potter's clay was mixed with distilled water in a blender to produce a thick slurry. The slurry was mixed with the sieved soil until a homogeneous mixture was obtained. The wet sediment was air-dried until damp and was then passed through a No. 5 sieve (2-mm) to produce an easily manipulated, coarse-powdered sediment that was allowed to air dry to constant weight at room temperature. Dried sediment was stored covered at room temperature, and autoclaved (20 min at 248° F, 15 PSI) prior to use.

2.3. Comparison of natural and synthetic sediments

2.3.1. Collection of natural sediments

Suitability of the synthetic sediment was assessed by monitoring survival and larval size after 90 d of rearing newly-hatched Hexagenia larvae (Hanes 1989) and by choice chamber experiments (Wright and Mattice 1981b). We compared Hexagenia development in the synthetic sediment with sediments from habitats known to be presently or historically suitable for Hexagenia development.

We collected natural sediments from six sites; Lake St. Clair (Anchor Bay, ANC); Balsam Lake (BAL); Lake Simcoe (Cook's Bay, COO); Georgian Bay (Honey Harbour, HON); St. Marys River (Lake Nicolet, NIC); and Lake Michigan (Saginaw Bay, SAG) (Table 1). Of these sites, the MOE frequently collects benthos for biomonitoring/bioassay at Honey Harbour (Hexagenia) and Balsam Lake (Elliptio mussels). The remaining four sites have historically supported large populations of Hexagenia.

Table 1. Summary of Sediment collection for 1989. The occurrence of Hexagenia larvae at the site at the time of collection is indicated.

Location	Code	Coordinates	Date (1989)	Amount (L)	Hexagenia
Honey Hbr., ON	HON	44° 50' N 88° 25' W	27 Aug	45	present
Balsam L., ON	BAL	44° 35' N 79° 49' W	27 Aug	45	present
Cook's Bay, ON	COO	43° 15' N 78° 29' W	28 Aug	45	absent
L. Nicolet, MI	NIC	46° 23' N 84° 15' W	17 Sept	45	present
Saginaw Bay, MI	SAG	44° 00' N 83° 40' W	17 Sept	45	absent
Anchor Bay, MI	ANC	42° 35' N 82° 44' W	20 Sept	25	present

At each of the six locales, sediment was collected using a mini-ponar grab (20 cm x 20 cm). Hexagenia and/or Chironomus (Diptera: Chironomidae) larvae occurred and were removed from the sediment in all samples. Sediment was returned to the laboratory in 15-L plastic buckets, autoclaved, and placed into cold storage (4° C).

2.3.2. Sediment composition

The particle size distribution of sediment samples (natural sediment from six sites + standard) was estimated by wet-sieving (coarse particle fraction) and hydrometry (silt and clay fractions; ASTM 1981). Mean organic matter content (4 replicates per sediment type) was determined by loss on ignition (550° C, 4 h) of oven-dried samples (105° C, 24 h).

Both natural and synthetic sediments were similar in inorganic particle size distribution but differed in organic content. All sediments consisted of 30-60 percent silt and 30-50 percent fine sand. The standard sediment had the greatest amount of organic material (ca. 28%), whereas sediment collected from Anchor Bay and Lake Nicolet had the least organic material (ca. 2%) (Table 2). Texture of organic materials differed between natural and the artifical sediments. Synthetic sediment contained primarily leafy and woody material characteristic of a littoral aquatic sediment. The natural sediments were dominated by fine, amorphous organic material typical of profundal regions.

2.4. Comparison of larval growth among sediments

The seven sediment types (see above) were each placed in standard rearing chambers and inoculated with newly-hatched Hexagenia larvae [natural sediments from 6 sites + standard sediment x 5 replicates/ treatment = 35 trials for 2 time periods (90 d, time to emergence)]. A density of 7 larvae per rearing chamber (1,000 larvae m^{-2}) was selected. This density allows rapid growth and low mortality while normally providing enough larvae for analysis of intrareplicate variability (Hanes and Ciborowski 1989).

Larvae were harvested from the appropriate containers after 90 d and preserved in 70% ethanol. Relative survival (proportion) was tabulated for each tank. Head width (HW), measured across the eyes, was determined for all larvae using an ocular micrometer in a dissecting microscope.

One-way analysis of variance (ANOVA) was used to test for differences in larval survival and size among the sediment types. If significant differences occurred, a Student-Newman-Keuls (SNK) multiple comparison test was used to determine which groups differed from one another.

Table 2. Mean (and 1 S.E.). amount of organic matter (percent) occurring in four replicate samples of each sediment type.

	Sediment Source						
	Anchor	Balsam	Cook's	Honey	Nicolet	Saginaw	Standard
Organic Content	2.38 (0.096)	18.55 (0.772)	11.94 (0.131)	4.09 (0.247)	2.14 (0.761)	8.89 (0.086)	28.21 (0.176)

2.5. Sediment preference

Two replicate seven-day sediment choice experiments were conducted to provide a measure of larval substrate preference. The choice-chamber was a 20-cm deep 56 x 56 cm plexiglass aquarium. An aluminum partitioning grid consisting of 49 (i.e. 7 x 7) cells (8 cm x 8 cm x 10 cm high) was placed within the square plexiglass aquarium. Seven aliquots of each sediment type (six field-collected sediments and standard sediment) were placed within the aluminum grid in a Latin Square configuration. Each sediment type was represented only once in a given row and in a given column of a grid of blocks so that no two blocks of the same sediment type were adjacent. The arrangement of the sediment was changed between replicates such that all combinations of adjacent sediment types were examined. The sediments had been kept in cold storage for approximately 18 weeks at the time the experiment began.

Approximately 250 mL of sediment was added to each cell (ca. 5 cm depth). Aerated, distilled water was added to the tanks to produce a depth of 13 cm over the sediment). One mL of concentrated food mixture was added to each cell and stirred into the sediment. The aquarium was aerated for one week prior to addition of larvae (Hanes 1989).

Test organisms had been reared in the standard sediment at a density of 8 larvae per 63-cm^2 rearing chamber (1270 larvae m^{-2}) for six months prior to the experiment (mean length ± 1 S.E. = 12.77 mm ± 0.256, n = 382). Eight larvae were placed within each cell. The aluminum partitioning grid was removed after 1 h and replaced 7 days later (Wright and Mattice 1981b). *Hexagenia* larvae were recovered and enumerated by passing the sediments within each partition through a 500-µm sieve. Larval size (head width across the eyes) was subsequently determined.

3. RESULTS AND DISCUSSION

3.1. Viability and variation among hatching eggs

Approximately 90 - 95 % of all eggs hatched whether or not they were previously placed into cold storage. Eggs maintained at room temperature immediately after collection began to hatch after 14 days. Cold-stored eggs required 6 d at room temperature prior first hatching. Almost all hatching occurred over a 4 d interval regardless of storage method.

Of the eggs that were refrigerated after having been left to hatch at room temperature, very few additional hatches were observed (< 0.01%). Therefore, it appears that delayed recruitment by overwintering plays a minor role in natural populations at this latitude (42°20'N). However, at more northern latitudes, it has been suggested that overwintering of eggs may be an important source of delayed larval recruitment (D. Giberson, pers. comm.).

In addition to providing us with adequate material for experimental rearings, the eggs collected from adult females are available for distribution to other laboratories. We feel that use of eggs from a single source will minimize test organism response variability among laboratories.

3.2. Larval growth and survival

After 90 d growth, survival significantly differed among the seven sediment types (ANOVA, $p < 0.01$). The Student-Newman-Keuls (SNK) test detected significant differences between two groups of sediment (Figure 1A). Although there was overlap in larval survival between the two groups, survival in SAG, NIC, COO and STND was significantly higher (60-90%) than survival in ANC, BAL, HON and SAG sediment (25-30%; $p<0.01$).

Larval size did not differ among the sediment types when mean HW for all larvae within a replicate tank was used for analysis ($F_{[6,19]} = 2.439$, $0.10 > P > 0.05$). However, loss of replicates per sediment type often resulted from high larval mortality. Complete larval mortality occurred in several tanks owing to chironomid infestations shortly after inoculation with Hexagenia larvae. The lost replicates substantially reduced the power of the analysis. Accordingly, the data were reanalyzed using individual HW of all larvae that survived within a particular sediment. Because there was significant variance added among replicates within treatments (nested ANOVA, $p < 0.05$) the pooling of larvae from different replicate tanks is not strictly valid. However, this procedure revealed strong differences in larval size among sediment groups (ANOVA, $F_{[6,90]} = 7.026$, $p < 0.001$). A SNK test revealed the presence of four overlapping groups of sediment that varied in larval size ($p < 0.05$; Figure 1B). BAL, STND and ANC sediments supported the smallest larvae; HON and SAG supported larvae that attained the largest size - over twice that of larvae in the smallest size group.

3.3. Sediment preference

To test the null hypothesis that larvae were distributed randomly among the sediment types, a two-way (sediment x trial) analysis of variance was conducted. We found a significant effect of sediment on larval density ($p < 001$). Although there was no difference in substrate selection between the two replicate trials ($p > 0.05$), there was a significant interaction effect between sediment type and trial. Although larvae consistently selected or avoided the same substrates in both trials, the response was more pronounced in one trial than in the other. The STND sediment contained the fewest larvae

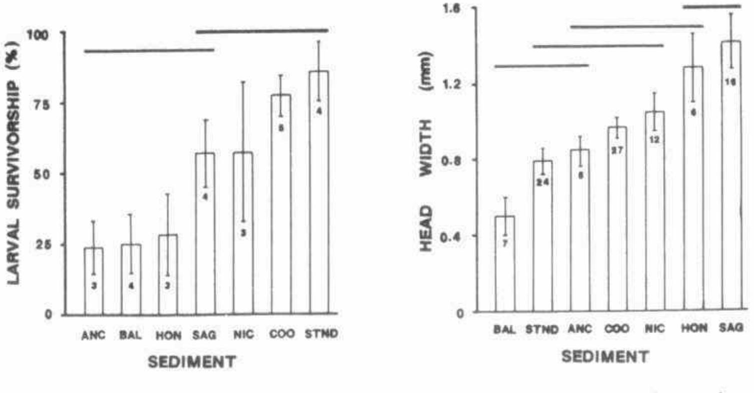

Figure 1. Mean (± 1 S.E.) survivorship and head width of larvae after 90 d growth on the different sediment types indicated. Solid horizontal lines connect sediments that did not differ from one another (SNK test, $p > 0.05$). ANC, Anchor Bay; BAL, Balsam Lake; COO, Cooks Bay; HON, Honey Harbour; NIC, Lake Nicolet; SAG, Saginaw Bay; STND, standard sediment. **A.** Survivorship. Numbers indicate the number of rearing tanks used in the analysis. **B.** Head width. Numbers indicate number of larvae used in the analysis.

($3.71 \pm 0.667/64$ cm^{2}cell; Fig. 2). NIC and BAL sediment harboured significantly more larvae per cell (6.57 ± 0.746 and 7.5 ± 0.769 per cell, respectively) than the STND sediment (SNK test, $p < 0.05$). The four remaining sediment types (SAG, ANC, COO and HON) contained the highest number of larvae per cell; their densities did not significantly differ from each other.

One-way ANOVA indicated that there was no significant difference in size (head width) of larvae among the sediment types ($p > 0.05$; $HW=1.51 \pm 0.11$ mm; body length = 12.77 ± 0.286 mm).

Examination of larval head band patterns (D. Giberson, pers. comm.) and male genitalia (visible through the larval cuticle; Burks 1953) indicated that 90 percent of larvae were H. limbata and 10% were H. rigida. There was no relationship between preferred substrate and species identity.

Our results suggest that rearing larvae on the STND sediment results in high survivorship. However, the individuals grow comparatively slowly relative to larvae reared in natural sediments. When given a choice among sediments, larvae appear to actively avoid the artificial sediment. We speculate that slow growth and avoidance responses are largely due to the low nutritional value of the organic component of the STND sediment (woody and leaf fragments). Accordingly, we have recently modified the STND sediment through addition of diatomaceous earth and food mixture to better mimic the fine particle distribution and overall organic content of natural sediments. Of the natural sediments examined, Saginaw Bay material was the most conducive to larval growth and survival. Comparative growth studies are in progress.

Other rearing chambers are being maintained until larvae reach maturity (i.e., emergence of subimagoes is achieved). We will evaluate median time (days) to emergence and biomass (a measure of fecundity; Boerger and Clifford 1975) as indicators of sediment suitability.

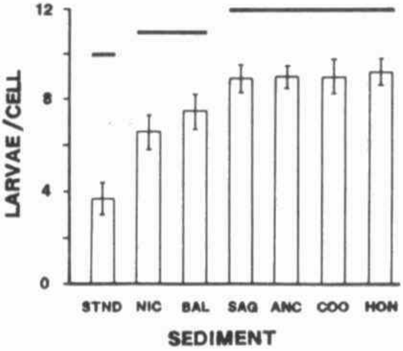

Figure 2. Mean (± 1 S.E.) number of larvae located in each sediment type within choice chamber after 1 week. Two trials were pooled for the analysis (n=14 cells per treatment). Solid horizontal lines join sediment types whose mean number of larvae do not differ from one another (SNK test, p>0.05). Abbreviations as in Figure 1.

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BP11

Tillage and Event Based Soil and Water Loss: Scale Linkages

R.G. Kachanoski*, W.T. Dickinson, and R. Rudra

University of Guelph and Waterloo Centre for Groundwater Research

University of Waterloo.

Soil erosion has been identified as a significant problem affecting water quality in Ontario. However, there have been few actual measurements. In addition the movement of dissolved chemicals in runoff water from agricultural land can also affect water quality. The variable, site specific nature of soil and water loss by runoff, as well as the lack of understanding of these processes under spatially varying field conditions has been documented.

Conservation tillage has been defined as any tillage system that reduces the loss of soil and water from a field. It is most often associated with minimum, non-inversion, or zero tillage systems. It is most often associated with minimum, non-inversion, or zero tillage system. The broad definition of conservation tillage is due to the recognition of significant interaction between specific soil types, climate, and tillage on runoff processes. Studies comparing one-time measurements of the effects of tillage on surface hydraulic properties may obtain contradictory results because the effects of tillage are time dependent.

Measurement of soil and water loss is difficult and is usually obtained from hillslope plots maintained over many years, or by rainfall simulation on microplots. Serious difficulties arise in attempts to transfer knowledge from laboratory or plot scale experiments to the field scale. Inability to cope with spatial variability remains a major obstacle to interpretation of research for field scale predictions.

The objectives of this study are to examine the spatial and temporal variations of soil and water loss under different tillage systems and soil types. Linkages between different spatial and temporal scales of measurement will be examined by measuring both event based losses at the plot scale, and average annual losses at the hillslope scale.

The project is being carried out on-Tillage-2000 plots. Tillage 2000 is a long term, on farm, field scale research and demonstration project initiated in 1985 by the Ont. Min. of Agric. and Food and the Dept. of Land Res. Science, Univ. of Guelph. Approximately 30 field scale sites with tillage comparisons have been established. Average annual soil loss is being measured at the hillslope scale using ^{137}Cs as a naturally occurring soil tracer.

Modified Rainfall Simulator

In order to examine the scale linkages between the plot scale (1m^2) and the landscape scale a modified version of the Guelph rainfall simulator was developed which allows the plot scale to be systematically increased or decreased. The new simulator system is composed of six (6) single nozzle rainfall simulators spaced evenly over a 1.6 x 10 m long plot. Each of the nozzles are connected to their own pressure regulator and solenoid control value. The pressure and solenoid switches are controlled by a single control board which allows the nozzles to be activated separately, or in combination as required.

A "simulation set" consists of turning on the first nozzle closest to the collection flume, and running the equivalent of a small plot scale simulation. After a preset length of time (usually 20 minutes), which is long enough for the runoff rate to reach steady state, the second nozzle is turned on and the simulation procedure repeated. This "scale up" of plot size is repeated for all size nozzles until the entire plot is being rained on. After the runoff rate for the six nozzle simulation reaches a steady state, the sequence is reversed with each of the nozzles being systematically shut off, and the steady state runoff, measured. Runoff rate and sediment loss from each spatial scale are collected along with detailed measurements of soil water content along the length of the plot from 25 installed Time Domain Reflectrometry TDR soil probes.

The sediment samples for all of the simulation runs are analysed for phosphorus, particle size distribution, and ^{137}Cs. The source soil from the runoff plots are also analysed for the same properties and sediment enrichment ratios are calculated.

At each of the runoff sites detailed measurements of surface roughness are being made in addition extensive measurements of the soil hydraulic properties are being made. These measurements were augmented by SWEEP-TED contract to test the new Guelph surface permeameter at the same runoff sites.

Results from the study indicated that no-till systems usually had higher runoff rates (lower infiltration) than the moldboard tillage system. However, the total soil loss and phosphorus loss from the moldboard treatment were higher. The runoff data is consistent with measurements of the hydraulic properties. The soil bulk density increased in the no-till with a subsequent decrease in total porosity. The decrease in total porosity was in macro-porosity which would account for the decreased infiltration. Measurements of saturated hydraulic conductivity and field saturated hydraulic conductivity were also significantly lower in the no-till system. The soil matrix flux potential was lower in the no-till system which along with higher initial soil water contents resulted in shorter predicted and measured time to ponding.

Scale Linkage

The similarity in the measured effects of tillage on the hydraulic and physical properties of the soil, and the measured relative differences in the runoff characteristics was encouraging. It suggested that relative runoff characteristics can be estimated from soil properties. However, a fundamental problem exists in trying to estimate absolute values of runoff characteristics. This problem is related to the problem of scale linkages and the fact that the hydraulic properties within landscapes are not single values, but rather a distribution of values with a specific probability distribution function.

a) Spatial Scale

The data indicated that the measurement of steady infiltration rate changed (increased) as the scale of the plot increased. the amount of change (scale dependance) was larger for the moldboard tillage system. The minimum plot size to encompass all of the infiltration variability (and thus obtain a scale independent value) will depend on the soil variability at the site, and the influence of the tillage system on the soil variability. The spatial variability of the hydraulic properties was usually significantly higher in the MB treatment. Thus, it is not surprising that the moldboard treatment was more sensitive to scaling.

(b) Rainfall intensity

The previous annual report mentioned the problem that changing the rainfall intensity changed the steady-state infiltration rate. At one site, as the rainfall rates changed from 4.1 cm/hour (low) to 16.8 cm/hour the measured steady state infiltration rate increased from 3.4 to 7.0 cm/hour. The effect of rainfall intensity can be explained by the variability of the soil hydraulic properties. For example, a soil with an average saturated hydraulic conductivity k_{sat} of 4.0 cm/hour should have an average steady-state infiltration rate of 4.0 cm/hour. However, if the rainfall rate were 4.0 cm/hour you would still get runoff because the 4.0 cm/hour infiltration rate is an average infiltration rate, and at least 1/2 of the plot must have a lower infiltration rate and would generate runoff. some of this runoff water will make it to end of the plot and be measured as runoff. Thus, the steady measured infiltration rate will be somewhat lower than 4.0 cm/hour. If you apply water at a higher rate the infiltration rate will increase because at least 1/2 of the area has a higher infiltration rate. Only when the entire area has been ponded will the infiltration rate become constant.

The use of physically based models to predict soil loss and surface runoff assume that smaller scale heterogeneity can be lumped into effective parameter values. The data from this study support recent theoretical studies suggesting it may be difficult to define effective hydrologic variables that will adequately represent the behaviour of a heterogeneous hillslope. If this is true, then physical models based on effective (average) hillslope properties have limited practical predictive value. Stochastic methods of linking observation at different scales are being examined.

BP12

VALIDATION OF SPOTTAIL SHINER DAILY OTOLITH RINGS

POWLES, P.M., B.A. POWLES, and R.A. CURRY.

Biology Department, Trent University, Peterborough, Ontario K9J 7B8

INTRODUCTION

This document reports to the Ontario Ministry of Environment our study on the ageing of spottail shiner (*Notropis hudsonius*). Although the grant's terms were addressed towards the spottail shiner, our attempts to collect that species met with little success in the early summer. However, we did capture on almost every occasion, the more common, bluntnose minnow (*P. notatus*). Since both species do overlap in their distribution, and are of comparable size in their first summer, we decided to include a comparison of age and growth for both species. The bluntnose minnow, however, appears to be a multiple (fractional) spawner, whereas the spottail does not, at least in our study site, 12-mile Lake.

The spottail shiner is used as a biomonitor of contaminants for the Great Lakes area, the body burden of metals and pollutants having been analyzed over a number of years by Karl Suns and his colleagues. To make the interpretation more accurate and more meaningful, Suns suggested that a knowledge of the precise ages of spottail (in relation to their size) would be most useful. Our intent was therefore, in this preliminary study, to assess the best method of ageing for DGIs (daily growth increments), and to validate the age and growth over the first summer from one study site. An accurate assessment of the size of "young-of-year" as opposed to 1+ fish was our first goal.

Only one other study has been carried out on the DGIs of cyprinidae, that of Victor and Brothers (1). They validated the age and growth of the fallfish (*Semotilus corporalis*), using the lapillus otolith (one of the 3 pairs of earbones found in bony fish.) Under a magnification of 400 - 1000x, this otolith clearly showed checks, yearly annuli, and DGIs. Because we obtained only a few eggs of spottail and reared them to validate the ages in days, we chose to follow length modes over time, and to inject fish with tetracycline to make a "mark" on the earbone as a reference point.

METHODS

A series of spottail shiners was collected randomly by seine from the same area in 12-mile Lake, Minden Co. These fish were preserved in 70% alcohol, measured, and the otoliths removed. A series of bluntnose minnows was also collected from Rice and Scugog lakes, and treated in the same way. Otoliths were mounted on slides, and viewed under 400x and 1000x with oil. The otoliths of fish over 4 cm in length required grinding, to elucidate the DGIs. Otherwise they were too thick to read accurately.

Modes in the length of fish and back calculations of the age in days were matched to the mean sizes in length. This method was successful for spottail, but since bluntnose is a fractional spawner, modes were less distinct. The otoliths of these two closely related species were very similar, although those of the spottail were rounder and the rings were more closely spaced than those of the bluntnose minnow.

RESULTS

For spottail, the changes in length modes over time showed that rings were laid down in a daily pattern. The back-calculated ages led to a hatch date of mid-May. Although spawning dates are not well documented, it is close to the observed date of spawning in Lake Simco (Ross, personal comm.) spawners, as opposed to the spottail, which spawn only once in 12-mile Lake (although this is possible they may spawn more frequently in their more southerly range.

In mid-July, most Y.O.Y.s ranged in length from 24-37 mm TL, and averaged 60 DGIs. By back calculation, hatch date was about mid-May. By August, average size was 36-54 mm TL, with ages corresponding to hatches of May 23, and May 29 (Table 1A). Within this size range there were also some yearlings in the catches.

Bluntnose minnows showed equally clear microzones, and back calculations suggested a May 15-20 for first hatch date period. (Table 2A) .

Figure 1A shows clearly the sizes of Y.O.Y. and 1+ bluntnose minnows were separated into modes in their length frequencies for mid-June to 22 July. By September, there was a wide range in the length frequency distribution, not so easily separable by modal peaks. On the basis of these modes and the growth curve, (not shown), the fish showed a logical sequence of increase in length in relation to days. The growth rates of both spottail and bluntnosed were quite similar.

By the end of the first summer, spottail in 12-mile achieved a length of 42 mm TL for young-of-year and over 50 mm TL for 1+, while available samples from southern Ontario for 1+ fish reached 6-7 cm TL. The smallest 1+ observed in July was 42 mm TL and by August, 60 mm. Thus, there is overlap. A preliminary key to the lengths of young-of-year fish of both species estimated from these data is shown below.

Table 1A. Spottail shiners ages in days (DGIs) for various dates, 12-mile Lake. 1988.

Sampling Date	DGIs (Average No.)	Mean TL	Hatch estimate
14 July 1988	53	24 mm	May 22
22 July 1988	58	30 mm	May 24
03 August 1988	70	32 mm	May 23
17 August 1988	76	42 mm	May 29

Table 1B. Y.O.Y. Age length key - Spottail shiner

Date of Capture	Kawarthas	Southern Ontario
Mid-July	under 4.0 cm TL	under 4.5 cm TL
3rd wk July	" 4.5 " "	" 5.0 " "
1st wk August	" 5.0 " "	" 6.0 " "
Mid-August	" 5.4 " "	" 6.5 " "

Table 2A Bluntnose Minnow Kawarthas Hatch Dates (approx) derived from DGIs.

Sampling Date	Average No. DGIs	Hatch Date
27 June 1988	45	May 15
22 July 1988	57	May 20

Table 2B Bluntnose minnow Y.O.Y. age length key, Kawarthas

End of June	Rice Lake	5.0 cm TL
End of July	Rice/Scugog	4.4 cm TL
End August	Rice	5.5 cm TL

DISCUSSION

There remain two aspects of the ageing biology of spottail shiner to be investigated prior to our complete satisfaction of the accuracy of the technique. There appeared to be subdaily rings on the otoliths of some fish, which resulted in a hatch date (after back calculation) which was unreasonably early. Injections of tetracycline and holding experiments are needed to solve this physiological question. Of seven small fish (8-11 mm TL) reared by Karl Suns from the eggs, and maintained for one month, the ages ranged from 35-40, which suggests excess daily rings in the early stages of growth. This confirmed our suspicion of the above. Secondly, a method should be developed to mark the annulus of otoliths so that they can be compared to the assumed annulus on the scales, which are far less tedious to read than otolith daily rings, but are more subject to "false annulus" formation.

ACKNOWLEDGEMENTS

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REFERENCES

1. Victor, B.C. and E.B. Brothers. 1982. Age and growth of the fallfish, *Semotilus corporalis*, with daily otolith increments as a method of annulus verification. Can. J. Zool. 60:2543-2550

(This is the only age study published on a freshwater cyprinid, using daily growth increments and relating the study to yearly annuli).

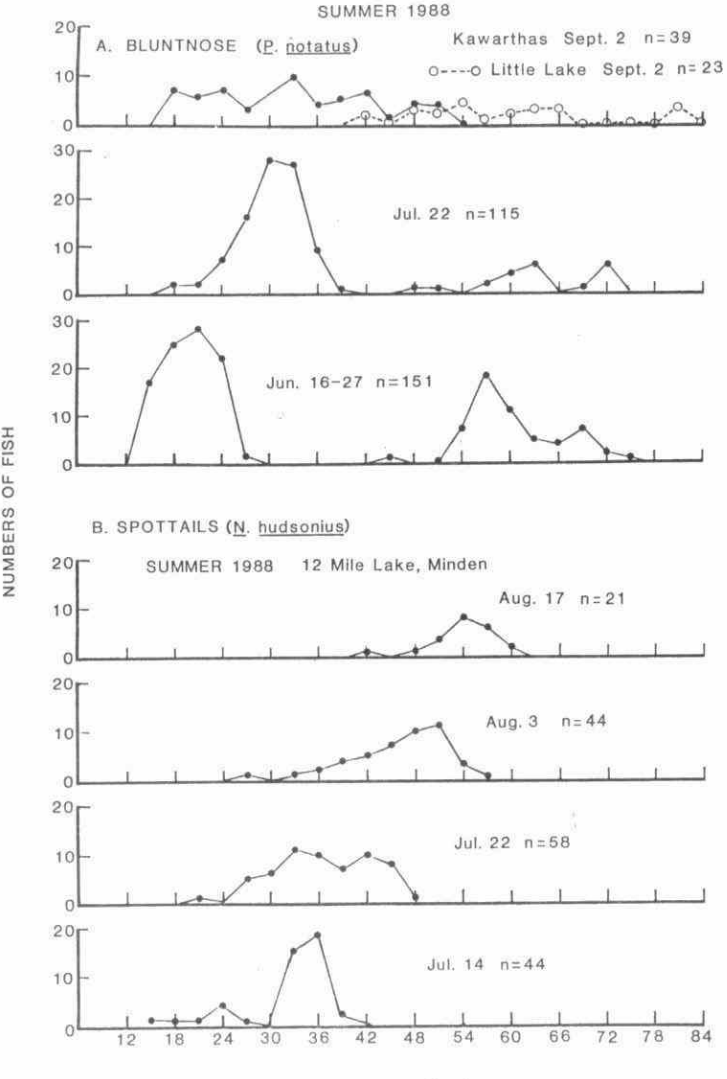

Fig. 1: Length of frequency distributions of bluntnose minnow and spottail shiner, 1988, taken by small-mesh beach seine.

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An Investigation of the Potential of Zygnematacean Zygospores, Peridinium, and Pediastrum as Paleo-indicators of Recent Lake Acidification.

*Zippi, Pierre, Y-K Yung, J.A. McAndrews, G. Norris and P. Welbourn, Institute for Environmental Studies, Department of Botany and Department of Geology, University of Toronto, Toronto, Ontario.

The increased growth of certain Zygnematacean algae in softwater lakes during the early stages of lake acidification has prompted an investigation of the potential use of zygospores of this family as paleoindicators of early acidification. The main purpose of the investigation was not to replace the transfer functions developed for diatoms and other siliceous scale-bearing Chrysophyceae, but rather to provide a more complete overview of past lake dynamics, especially in lakes where a clear relationship between diatoms, Chrysophyceae and pH cannot readily be established. Certain species of the filamentous green Zygnemataceae increase in abundance as pH drops to about 6.0. Zygospores have been described and in many cases can be used to characterize the species.

In the Fall of 1989, sediment cores were taken from 11 lakes in the Haliburton-Muskoka region of Ontario. To date, most of our effort has been directed to standardizing and testing techniques for the recovery and concentration of Zygnematacean zygospores from lake sediments. These zygospores are made of a sporopollenin-like substance, which is composed of oxidative polymers of carotenoids or carotenoid esters. The material is very resistant to decay and persists for millions of years in sediments.

The presentation will describe the steps developed for sample splitting, addition of marker grains, removal of carbonate, iron-oxy-hydroxide, and silicate minerals and fluoride by-products, removal of humic material and the removal of cellulose and hemicellulose by acetolysis. The flow chart below illustrates the steps for concentrating sporopollenin cysts from typical lake sediments.

1. Measure de-watered sediment volume
    2-3 ml of raw sediment exclusive of large vegetative or mineral fragments
    centrifuge at high speed to de-water sediment
    add known quantity of Lycopodium tablets – yields density: specimens/ml.
    Examine bulk sediment describe mineral and organic component.

2. Carbonate Removal – HCl
    removes calcareous algae, limestone and dolomite; dissolves tablets containing marker grains.

3. Humic acid removal – NH_4OH
    disperses organic floccules and removes humic material, oxidized cellulose, clay- sized amorphous mineral and organic particles.
    Examine general relationships between all fossil groups (except calcareous algae).
    Sample cut for diatom analysis.

4. Silica and silicate removal – HF
    removes diatoms, sponge spicules, and silicate minerals.
    Examine cellulosic remains, many types of algae preserved.
    Sample cut and slides made for algal analysis.

5. Acetolysis – H_2SO_4: $(CH_3CO)_2O$ (1:9)
   removes cellulose and hemi-cellulose.
   Make final slides for analysis.
   Only "sporopollenin" remains;
   spores, pollen, dinoflagellates, pediastrum, and
   zygospores.

Zygnematacean zygospores are more resistant to oxidizing acids than most types of pollen. Further concentration of Zygnematacean zygospores from the overwhelmingly abundant pollen may be possible by controlled oxidation of the residue. Attempts at concentrating Zygnematacean zygospores by oxidation with chromic acid and nitric acid have both show promising results, but has not resulted in a practical method for yield a statistically reliable concentration of zygospores.

Preliminary results suggest that while the frequency of Zygnematacean zygospores may limit their usefulness as paleoindicators of acidification, nevertheless, other algal cysts formed of sporopollenin, especially *Pediastrum* spp. and *Peridinium* spp. may be more useful, since they exhibit clear pH preferences over the range of interest, and are more abundant than the Zygnematacean spores in the samples which have been studied to date.

Over 40 types of acid-base-acetolysis resistant (mostly algal) cysts were encountered in the organic residues that were concentrated from the lake sediments. Table 1 illustrates reconnaissance level results for the abundance of cysts of the dinoflagellate genus *Peridinium* and coenobia of *Pediastrum*. Cysts of *Peridinium* can readily be identified to species level for at least 4 species. Coenobia of *Pediastrum* can be identified to species and often varietal level. A general relationship of higher diversity of *Peridinium* cysts and lower diversity of *Pediastrum* coenobia to decreasing pH values is apparent in Table 1. Cysts of *Peridinium limbatum* and *P. wisconsinense* are associated with lower pH lakes, while common occurrences of most species and varieties of *Pediastrum* occur in lakes with higher pH. Ongoing quantitative analysis will show if a successful paleo-indicator of pH may be derived by using a combination of diversity measures and pH-related species entry levels for *Peridinium*, *Pediastrum* and several types of green algae with cell walls formed of sporopollenin.

Lake	pH	Microflora recovered from surface sediments ——>													
		Peridinium				*Pediastrum*									
		limb	wisc	bipes	willeii	araR	bory	borL	borS	dupl	dupC	inte	intP	intS	Zygs
Leonard	5.5	A	A	C	P	P									
Plastic	5.7	AA	C	C	C										P
Tock	6.4	C	C	C	P	C		P							?
St. Nora	6.6	C	C	C	P										?
Rabbit Bay	6.7		P	P	C										
Kushog	6.8			P	C	C	P								
Harp	6.8				C							C			P
Little Clear	6.9			C	C	C	C					P	P		
4 Mile	7.8			C	C		C		C	C					P
White	8.7				P		C				C	C		C	

Table 1 - Reconaissance tabulation of algal cysts recovered from surface samples from 10 lakes in the Haliburton—Muskoka region of Ontario during the Fall of 1989.

Legend for Table 1:

Peridinium
limb= P. limbatum
wisc.= P. wisconsinense
bipes= P. bipes
willeii= P. willeii

Pediastrum
araR= P. araneosum rugulosum
bory= P. boryanum
boryL= P. boryanum longicorne
boryS= P. boryanum (smooth)
dupl= P. duplex
dupC= P. duplex clathratum
inte= P. integrum
inteP= P. integrum priva
inteS= P. integrum scutum

Zygnemataceae
zygs= smooth wall ellipsoidal zygospores unidentifiable at genus level.

AA= very abundant
A= abundant
C= common
P= present

Core samples from Plastic lake are currently being analyzed for *Peridinium* cysts, *Pediastrum* coenobia and other types of sporopollenin based algae cysts. Paleo-environmental interpretations will be made from relationships determined from the analysis of surface samples from lakes listed in Table 1.

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